51 – 2

POLYMORPHIC TRANSFORMATIONS OF SOLIDS UNDER PRESSURE
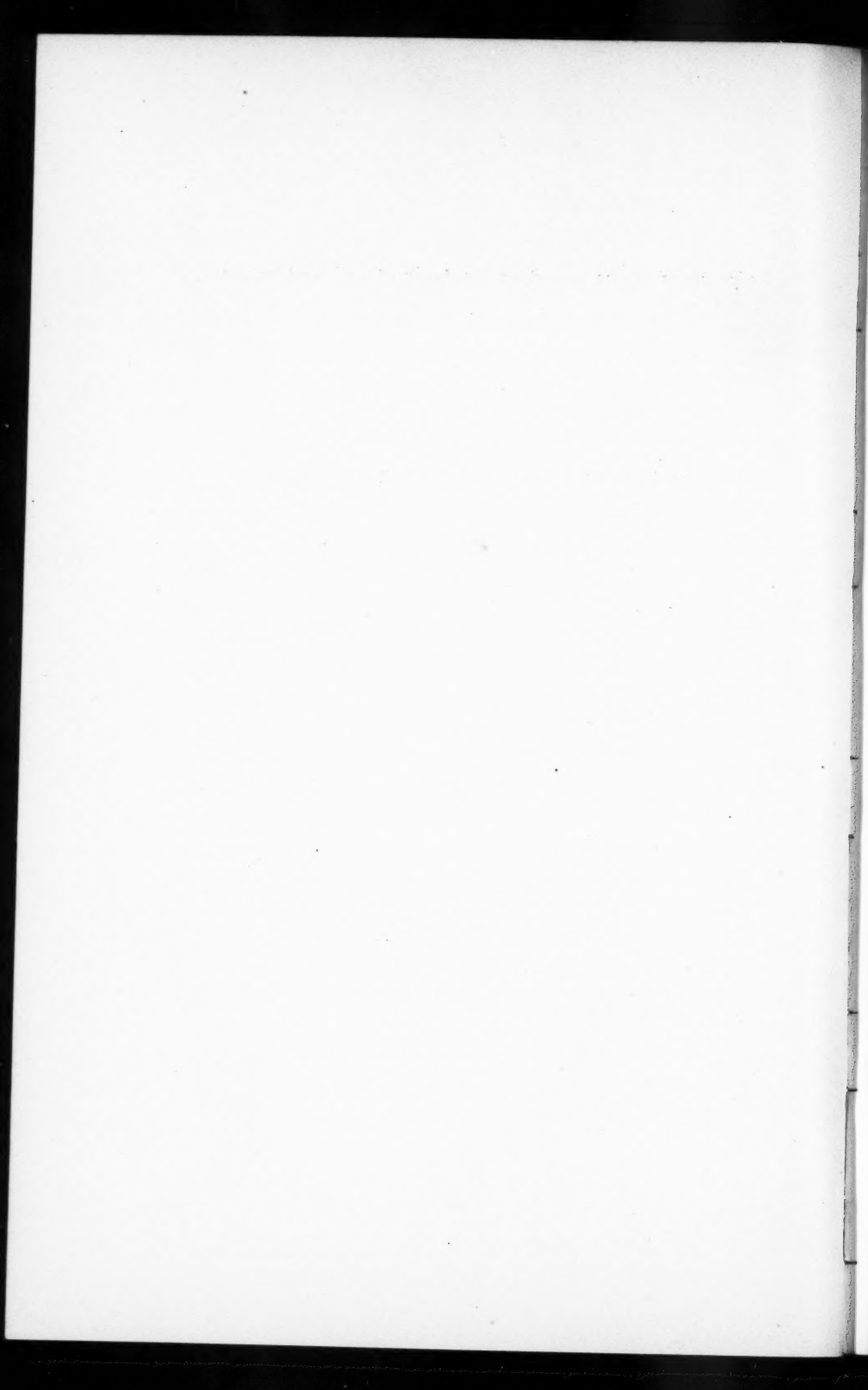
By P. W. Bridgman.

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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL
LABORATORY, HARVARD UNIVERSITY.

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CONTENTS.

INTRODUCTION.

IN this paper data are given sufficient for a thermodynamic specification of a number of polymorphic transitions between solids. Besides the transition quantities themselves (change of volume, latent heat, slope of the transition line) it has been possible in a good many cases to give at least a rough approximation to the difference of compressibility, thermal expansion, and specific heat of the reacting phases. The field is a comparatively unworked one. Hitherto investigations on polymorphic changes have been concerned for the most part with the temperature of transition at atmospheric pressure. There are not many measurements of latent heat or change of volume even at atmospheric pressure. Still fewer measurements of the effect of pressure have been made; many of these are due to Tammann, whose pressure range was considerably lower than that of this paper. The

range of this paper is from 0° to 200°, and from 1 to 12000 kgm.   The measurements to be given here must be regarded as only the beginning of an attack on an immense field.   The most important immediate task would seem to be the collection of a large mass of data, so that we may become familiar with the general types of phenomena.   About the only discussion that can be attempted is a thermodynamic one, and even from this narrow point of view the measurements are not sufficient to completely determine the behavior of the several phases. We can go only a little way toward the solution of the general problem, which is to predict from the properties of any one phase when to expect new polymorphic phases, and what their properties will be.   We may perhaps expect more definite results when methods such as are used here are taken in conjunction with recent X-ray methods for determining crystal structure.

Thermodynamically, the transition between two solids is characterized by the same elements as determine the melting and the vaporization curves, and from this point of view the discussion of previous papers [1] is applicable.   As a matter of fact, however, the character of the solid-solid curves may vary much more widely than that of the melting or vaporization curves.   For instance, all vaporization or melting curves, absolutely without exception, either rise or fall over their entire length, while solid-solid curves may have either a maximum temperature or pressure.   In the previous discussion it was not necessary, therefore, to consider certain special relations between the thermodynamic constants at the maximum points, but now these relations become of importance.   A discussion of these is given in the following.   Another matter that needs reconsideration is that of the effect of impurities at a point of maximum pressure.   Evidently the usual statement of the effect of impurity as causing a displaced temperature of equilibrium will not serve here.   In the following are given the slight modifications necessary in the usual discussion to find the pressure shift of the equilibrium line.

It has been possible to give a much more thorough investigation of the difference of compressibility, thermal expansion, and specific heat between the several phases than was possible in the case of melting. The reason for this is the much greater reliability of the experimental measurements of the difference of compressibility between the separate phases, because, except in those cases where the impurity forms mixed crystals, there is absolutely no rounding of the corners of the volume-

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1 P. W. Bridgman, Phys. Rev. **3**, 126–203 (1914), and **6**, 1–33 (1915).

pressure isothermals preliminary to a reaction. Furthermore, in the case of those substances whose phase diagrams contain triple points, it is possible to calculate completely the three differences from the thermodynamic data of the transition curves alone.

Among the data which do not enter into the thermodynamics of phase change, but are nevertheless of significance for the mechanism of the transition, may be mentioned the amount of superheating or subcooling a phase will support, the velocity of transition, and the width of the band of indifference. To determine these data so as to have absolute significance is a matter of great experimental difficulty, since slight impurities and the character of the apparatus produce great changes in the measured effects. No such measurements have been attempted in this work. Nevertheless a number of qualitative and comparative measurements have been made incidentally in the course of the measurements, which are of orienting value. Since these measurements are so different in their character from the thermodynamic measurements which form the bulk of this paper, it has seemed best to reserve most of them for another paper.

This paper is the first of several which are to deal with solid transitions under pressure. In this first paper I will give the preliminary thermodynamic discussion which will be necessary to all the work on solid transitions, and also data for a number of such transitions. Discussion of the data may be profitably left for later papers, after a greater mass of data has been presented.

EXPERIMENTAL PROCEDURE.

The procedure was, except for some minor details, like that of two previous papers.[1] The most important difference is in the receptacle for holding the substance under investigation. Most of the substances were solid throughout the range of investigation. If the substance was one not dissolved by kerosene it was usually rammed dry into a thin shell made of a piece of steel tubing, open at both ends, the tubing just fitting the inside of the pressure cylinder. The shell was held in a heavy steel form during the filling, so that it should not be bulged by the ramming into place of the material, which was accomplished with a steel piston and a heavy hammer. Frequently after the shell had been filled, numerous holes were drilled laterally through the walls, to procure as ready access as possible by the kerosene to all

parts of the mass. It might at first thought seem that the steel shell would produce irregularities by tending to hinder the change of volume accompanying the reaction, but no irregularities of this nature were ever found. Sometimes, when the substance could be melted without danger of decomposition, it was melted, instead of hammered, into the shell. Under these conditions the shell was, of course, closed at the bottom end. If the substance were one soluble in kerosene, two slightly different methods were used. By the first method, the salt was formed into a cylinder of suitable dimensions, either by ramming into a split mound or by melting into a form, and then submerged under mercury in a steel shell, being prevented from rising by a clip at the upper end. Or it might be hammered or melted into a steel cylinder, which was then inverted below the surface of mercury as shown in Figure 1. This method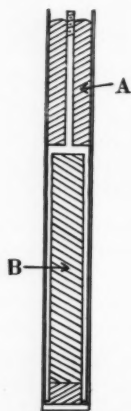 is applicable if the substance melts somewhere within the range of the experiment, and was used in all such cases. The air, of course, was exhausted in this case. The chief trouble with this method of the inverted cup is that the cup is very likely to be ruptured by the change of volume during either melting or the change from one solid to another. Substances are strikingly different in their rigidity and the readiness with which they rupture the cylinder. It is significant that the shell was never ruptured while determining transitions in the low pressure apparatus; this is another bit of evidence showing the greatly increased rigidity, or better, viscosity, produced by high pressures. The shells finally had to be made of hardened chrome nickel steel of the dimensions shown, and even then they were sometimes broken. The dimensions of the free space allowed for the mercury are of importance, since the kerosene must not come in contact with the substance in consequence of the changes of volume brought about by the transitions or the compressibility. The proportions shown sufficed for all substances investigated here up to 12000 kgm.

FIGURE 1. The modified form of container for those substances which melt within the range of the experiments.

In other respects the apparatus was of the same design as that previously used, but accidents necessitated the renewal of various parts. Three lower cylinders were ruptured, two by amalgamation, and one by a violent explosion. This explosion also ruined

the upper cylinder and the connecting tube.   If any one should ever have occasion to do work similar to this again, he should use every precaution when working with mercury salts.   These decompose slightly in contact with the steel, and deposit free mercury, which gradually works its way through the cylinder, even when it is 5 inches in diameter, as was that used here.   The flaws which resulted from this action of the mercury were not traced to their true cause until two cylinders had been ruptured.   The coils with which pressure was measured were also replaced a number of times.   These were frequently destroyed when the substance under investigation decomposed at the higher temperatures and the decomposition products found their way to all parts of the apparatus.   Fortunately a number of well seasoned coils were in hand, so that new ones could be substituted and measurements immediately begun without waiting for seasoning. The new coils were always calibrated in the way already described by determining the melting point of mercury at 0°.

The materials were obtained in as pure a state as possible from various chemical houses, and used in most cases without further purification except careful drying.   However, those organic substances which had a convenient melting point were further purified by crystallization in a thermostat at constant temperature.   Slight impurity is of very much less importance in the case of solid transitions than it is for melting, because here the transition coördinates are not affected except in those rare cases where mixed crystals are formed.   At least one such case was noticed, however.

The Effect of Impurities on the Transition Lines.

In an earlier paper [1] a deduction was given of the temperature depression of a transition point which was applicable at any pressure, since it did not involve the assumption of a vapor phase, as such deductions usually do.   To find how a whole transition line is affected by impurity, one has only to apply the formula given there to every point in order to obtain the equation of the modified line in terms of a displacement at every point parallel to the temperature axis.   But this process evidently fails if the transition line itself is parallel to the temperature axis.   Such transition lines do not occur for melting, but they are comparatively common for solid transitions, and it becomes important to find another expression for the shift of the equilibrium line.

The formula is readily derived by the thermodynamic potential. We first derive again by this method the ordinary expression for the temperature depression, since it is very easily done, and may perhaps make matters a little clearer. Let us suppose that pure (1) and (2) are in equilibrium at p, t on the transition line. (See Fig. 2.)
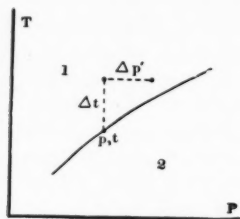

FIGURE 2. Showing the displacement of pressure and temperature produced by impurities.

Then we know that at this point the thermodynamic potentials are equal, or $Z_1 = Z_2$. Let us now subject the phase (2) to a temperature increment ($\Delta \tau$) only, but the phase (1) to a simultaneous temperature increment ($\Delta \tau$) and pressure increment ($\Delta p'$). We demand that $\Delta \tau$ and $\Delta p'$ be so chosen that (1) and (2) are in equilibrium under the new conditions, that is, $\Delta Z_1 = \Delta Z_2$. We have in general

$$\Delta Z = \left(\frac{\partial Z}{\partial \tau}\right)_p \Delta \tau + \left(\frac{\partial Z}{\partial p}\right)_\tau \Delta p$$
$$= - s \Delta \tau + v \Delta p$$

Now if $\Delta p'$ is chosen as the negative of the "osmotic pressure" of impure (1), it is obvious that impure (1) at p, $\tau + \Delta \tau$ will be in equilibrium with pure (1) at $p + \Delta p'$, $\tau + \Delta \tau$, and that hence the impure (1) will be in equilibrium with pure (2), where now pressure and temperature are the same on both impure (1) and pure (2), as they actually are. We have, therefore,

$$- s_1 \Delta \tau + v_1 \Delta p' = - s_2 \Delta \tau$$
$$\Delta \tau = \frac{v_1 \Delta p'}{s_1 - s_2} = - \frac{\tau v_1}{\Delta H} \Delta p$$

where $\Delta p \ (= -\Delta p')$ is the osmotic pressure of the impurity. This is the formula derived in the previous paper, except for sign. Δp is

always positive; hence $\Delta\tau$ is negative, and the transition line is depressed.

The procedure is easily modified so as to give the pressure shift of the equilibrium line. Let now the pressures only be altered. The pressure on (2) is increased by Δp_2, and that on (1) by Δp_1. (See Fig. 3.) Under these conditions pure (1) at $p + \Delta p_1$, τ is to be in

FIGURE 3. Showing the displacement of pressure produced by impurities.

equilibrium with pure (2) at $p + \Delta p_2$, τ. If now we choose $\Delta p_2 - \Delta p_1$, equal to the osmotic pressure of the impurity dissolved in (1), then we have impure (1) at $p + \Delta p_2$, τ in equilibrium with pure (1) at $p + \Delta p_1$, τ, and hence in equilibrium with pure (2) at $p + \Delta p_2$, τ. That is, Δp_2 gives the pressure shift of the transition line.

We have

$$\Delta Z_1 = \Delta Z_2$$

or

$$v_2 \Delta p_2 = v_1 \Delta p_1$$

also

$$\Delta p_2 - \Delta p_1 = \Delta p \qquad (\Delta p = \text{osmotic pressure})$$

Whence

$$\Delta p_2 = \frac{v_1}{v_1 - v_2} \Delta p$$

This gives the pressure shift ($= \Delta p_2$) of the line due to impurity. It might have been obtained from the value given above for the temperature shift by putting $\Delta\tau = \dfrac{d\tau}{dp} \Delta p$, but the method of deduction there given did not make it evident that this substitution would be allowable when $\dfrac{d\tau}{dp} = \infty$, as it is in those cases to which we wish to apply the

formula. Conversely, of course, the formula for the pressure shift does not apply at a horizontal part of the transition line, where $v_1 - v_2 = 0$.

These formulas have been subjected to no restriction in the derivation except that the phase (1) is that in which the impurity is dissolved. This might, if we liked, be the phase stable at the higher pressure or the lower temperature, instead of as we have shown it. The formulas show that in all cases the effect of impurity is to shift the transition line into the region of the pure phase. For a given concentration of the impurity, that is, for a given osmotic pressure, the displacement is greatest for those substances with a small latent heat and a small change of volume. These are much smaller for the solids investigated here than for liquids, so that one would expect in general the displacement of the transition lines to be greatest for the substances investigated here. But as has been remarked, very few of these substances contain dissolved impurities (form mixed crystals), so that most of the transition lines are unaffected by what impurities there may be.

If the impurity is soluble in both phases, we get for the pressure shift

$$\Delta p = \frac{v_1 \Delta p_1 - v_2 \Delta p_2}{v_1 - v_2}$$

and for the temperature shift

$$\Delta \tau = - \frac{\tau}{\Delta H} \left[v_1 \Delta p_1 - v_2 \Delta p_2 \right]$$

This shows that if the total amount of impurity is slight, and if it is so distributed between the two phases that $v_1 \Delta p_1 = v_2 \Delta p_2$, then there is no shift of the transition line.

The phenomena in the neighborhood of a triple point offer no particular difficulty. It may be shown directly by substitution that the displaced transition lines must pass through a triple point as well as the original lines, no matter what the relative amounts of impurity dissolved in the three separate phases. This of course is what we know must be the case from other considerations.

It should be noticed that although these formulas are entirely valid when the impurity is dissolved in more than one phase, nevertheless the conditions under which they are derived are not always close to the conditions of practise. We have assumed a knowledge of Δp_1 and Δp_2. This demands that we know the way in which the impurity is divided between the two phases. In practise this problem of the distribution of the impurity must usually be solved first, since the

practical conditions usually give us the total amount of impurity present in the two phases together. The distribution problem is not touched above; to solve it would require a knowledge of the heat and volume effects of solution.

The Equation of the Transition Lines.

This equation has already been developed in a previous paper.[1] The equation is

$$(p - p_0)\left[\Delta v + \Delta \beta\, (\tau - \tau_0) - \tfrac{1}{2}\Delta a\, (p - p_0)\right] - (\Delta s_0 - \Delta C_p)\, (\tau - \tau_0)$$

$$- \Delta C_p\, \tau\, log\, \frac{\tau}{\tau_0} = 0$$

For the slope of the line we find

$$\frac{d\tau}{dp} = \frac{\Delta v_0 + \Delta \beta\, (\tau - \tau_0) - \Delta a\, (p - p_0)}{\Delta s_0 + \Delta C_p\, log\, \dfrac{\tau}{\tau_0} - \Delta \beta\, (p - p_0)}$$

and for the second derivative

$$\frac{d^2\tau}{dp^2} = -\frac{1}{\Delta v}\,\frac{d\tau}{dp}\left[\frac{\Delta C_p}{\tau}\left(\frac{d\tau}{dp}\right)^2 - 2\,\Delta\beta\,\frac{d\tau}{dp} + \Delta a\right].$$

The notation is as follows; Δv is the difference of volume of the two phases at the point p_0, τ_0 of the transition line ($\Delta v = v_1 - v_2$). $\Delta \beta$ is the difference of the thermal expansions.

$$\Delta \beta = \left\{ \left(\frac{\partial v_1}{\partial \tau}\right)_p - \left(\frac{\partial v_2}{\partial \tau}\right)_p \right\}$$

Δa is the difference of the compressibilities considered as positive.

$$\Delta a = -\left\{ \left(\frac{\partial v_1}{\partial p}\right)_\tau - \left(\frac{\partial v_2}{\partial p}\right)_\tau \right\}.$$

ΔC_p is the difference of the specific heats ($\Delta C_p = C_{p_1} - C_{p_2}$), and Δs_0 is the difference of entropy between the two phases ($\Delta s_0 = \Delta H/\tau_0$). The equation presupposes that throughout the range of application Δa, $\Delta \beta$, and ΔC_p remain constant.

In the preceding paper very little discussion was given of the shape of the curve determined by the above equation, because the shape of the melting curve is determined essentially by the variations with pressure and temperature of $\Delta \alpha$, $\Delta \beta$, and ΔC_p. In particular, $\Delta \alpha$

varies greatly over the pressure range of 12000 kgm. But in the case of the solids to be studied here, it seems reasonable to assume a considerably better approach to constancy of the three differences. For instance, the compressibility of a liquid such as water has decreased to $\frac{1}{5}$ its initial value at 12000 kgm., whereas the compressibility of steel does not vary more than a fraction of one per cent over the same range. Steel is of course an extreme case, and the difference of compressibility may change much more than the compressibility, but in any event we would seem to be justified in presuming that $\Delta\alpha$ for two solids is more constant than for a solid and a liquid. A discussion of the above equation is of more value here, therefore, than in the case of the melting curves. It will not pay to completely discuss all possible combinations of the constants. We will, however, show that the curve may take a great variety of shapes according to the relations between the constants, and that some of these shapes do not seem to exist in practise. We infer, therefore, that in practise the constants do not assume all possible relations to each other; it will be our problem in the latter part of this paper to determine these constants, and find within what relative range they are actually restricted.

We notice in the first place that if $\Delta\alpha > 0$, that is, if the high temperature phase is more compressible, as it is in many cases, that the curve crosses the pressure axis twice. For we obtain immediately on putting $\tau = \tau_0$ that $p - p_0 = \dfrac{2\,\Delta v}{\Delta\alpha}$. This means that when the pressure has been increased sufficiently to squeeze the high temperature phase into a volume as much smaller than the low temperature phase as it was originally larger, the two phases can coexist again in equilibrium. This in itself indicates a rather unusual state of affairs; the only example found so far is HgI_2. But the equation furthermore indicates that the curve may under proper conditions break up into two curves, the second pressure just found lying on the second curve. This would mean that the same phase may exist in two isolated regions of the phase diagram, the two regions of stability being separated by the region of stability of the second phase. Such cases, if they occur at all in practise, are extremely rare; the only suggestion of such a thing of which I know is concerning the modification of NH_4NO_3 stable below $-16°$, made by Wallerant.[2] This however has not been verified in a more recent very careful investigation by Behn,[3] although

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[2] F. Wallerant, Bull. soc. fr. min. 133–374 (1905).
[3] U. Behn, Proc. Roy. Soc. **80**, 444–457 (1907–08).

he was not able to prove definitely that such was not the case. It is
interesting to bear in mind that this is at least a theoretical possi-
bility. For the present, then, we shall assume that $\Delta\alpha$ does not
remain constant over a wide enough range to allow curves with two
branches, and we shall consider only the nearer branch of the curve
in the following.

If the two phases have the same specific heats ($\Delta C_p = 0$) the equa-
tion becomes particularly simple, degenerating into a hyperbola. This
hyperbola has one vertical asymptote and one inclined at an angle
$\dfrac{\Delta a}{2\,\Delta\beta}.$ The hyperbolic form includes a number of types of behavior.
If $\Delta\alpha > 0$, the curve may rise to a vertical asymptote, or may rise to a
maximum and fall to a vertical asymptote, or rise to a maximum and
fall to an inclined asymptote, or fall to a vertical asymptote, or fall
to a minimum and rise to a vertical asymptote, or fall to a minimum
and rise to an inclined asymptote.   And if $\Delta\alpha < 0$, the curve may rise
to a vertical asymptote or rise to an inclined asymptote with con-
vexity either up or down, or may fall to a vertical asymptote, or may
fall to an inclined asymptote with convexity either up or down.   Of
these cases, at least those with a vertical asymptote do not appear to
occur in practise. The hyperbola degenerates into one important
special case.   If $\Delta C_p = 0$, and $\Delta\alpha = 2\Delta\beta\,\dfrac{d\tau}{dp}$, the curve breaks up into
two straight lines (we neglect the second line).   Many of the transi-
tion lines actually found are nearly straight, so this condition is ap-
proximated to in practise.

If now, in general, $\Delta C_p \neq 0$, we see that the curve can never have a
vertical asymptote.   It may, however, have a vertical tangent, and
be double valued with respect to temperature, if $\Delta C_p < 0$.   This is a
case met in practise, benzol and ice for example.   In general the
equation demands at high pressures either a maximum or a minimum,
or a curve with two branches.   Since these are not actually of frequent
occurrence, the legitimate use of the equation must be restricted to a
comparatively narrow pressure range. We may perhaps say that very
roughly the usual type of the curve is one concave toward the pressure
axis, whether rising or falling.   If the curvature is reversed, and there
are examples of this, it would imply in general either an exceptionally
large positive value of $\Delta\beta$, or a negative value of ΔC_p.

We discuss now the relations at a horizontal or vertical tangent.
We have seen in the previous paper that the transition data give us two
relations between $\Delta\alpha$, $\Delta\beta$, and ΔC_p.   In general one other relation

is necessary to compute these three quantities. But at a horizontal or vertical tangent, the relations simplify in such a way as to determine uniquely two of these three quantities without the necessity for a third relation. We shall assume for the deduction that we know ΔV and ΔH along the transition line. These date are, as a matter of fact, determined in the following work. We are at liberty there-fore to use the following relations:

$$\frac{d\Delta v}{dp} = \frac{d\tau}{dp}\Delta\beta - \Delta\alpha$$

$$\frac{d\Delta H}{dp} = \frac{d\tau}{dp}\Delta C_p + \Delta v - \tau\Delta\beta$$

Now at a horizontal tangent, $\frac{d\tau}{dp} = 0$. We immediately see that at such a point the equations give us the means of determining both $\Delta\alpha$ and $\Delta\beta$ from the transition data alone. These values are;

$$\left.\begin{array}{l} \Delta\alpha = -\dfrac{d\Delta v}{dp} \\[3mm] \Delta\beta = -\dfrac{1}{\tau}\dfrac{d\Delta H}{dp} \end{array}\right\}$$

We cannot find ΔC_p from the equations; the only method is direct experimental determination. These relations are of application to HgI_2. The equations furthermore show that for those substances which we may call normal $[\Delta\alpha>0, \Delta\beta>0]$, the maximum of the ΔH curve must come before the maximum of the transition curve.

At a vertical tangent, $\frac{dp}{d\tau} = 0$, and we get

$$\left.\begin{array}{l} \Delta C_p = \dfrac{d\Delta H}{d\tau} \\[3mm] \Delta\beta = \dfrac{d\Delta v}{d\tau} \end{array}\right\}$$

These relations are of application to water or benzol. We cannot determine $\Delta\alpha$ at a vertical tangent from the transition data alone.

Two of the relations may be written in a simpler form, involving the curvature of the transition line. These relations are;

$$\Delta\alpha = -\frac{\Delta H}{\tau} \times \text{curvature, at a horizontal tangent} \left(\frac{d\tau}{dp} = 0\right),$$

and

$$\Delta C_p = -\tau\Delta v \times \text{curvature, at a vertical tangent} \left(\frac{d\tau}{dp} = \infty\right).$$

It is to be noticed that either a horizontal or a vertical tangent demands properties that are in a certain sense abnormal. At a horizontal tangent, to the right of the point of tangency, the phase with the smaller volume has the higher compressibility, and immediately below a vertical tangent the phase stable at the higher temperature has the smaller specific heat. We have examples for both these cases.

We have seen that it is not possible in general to determine $\Delta\alpha$, $\Delta\beta$, and ΔC_p from the data of the transition curve alone. (By the transition data we mean the curve giving the relation between pressure and temperature, and the values of ΔV and ΔH along this curve.) It is important to notice, however, that if the three phases come together to a triple point, we do have enough to determine $\Delta\alpha$, $\Delta\beta$, and ΔC_p completely on each of the three transition lines. The reason for this is that $\dfrac{d\,\Delta v}{dp}$ and $\dfrac{d\,\Delta H}{dp}$ are independent of each other on the three lines, whereas $\Delta\alpha$, $\Delta\beta$, and ΔC_p are not. We have evidently $\Delta\alpha_{13} = \Delta\alpha_{12} + \Delta\alpha_{23}$ etc. That is, at a triple point there are only six unknowns to determine, and six equations, one involving $\dfrac{d\,\Delta v}{dp}$ and another involving $\dfrac{d\,\Delta H}{dp}$ on each transition line. The six equations are obvious from the above; we need not bother to write them down. This information is most important. In the following the results of the calculations are given for those substances whose phase diagrams contain triple points.

In the case of those substances which do not have a triple point it has been possible in a good many cases to obtain some evidence as to the value of $\Delta\alpha$ from the difference of slopes of the isothermal p–v lines above and below the transition point, and so, with the equations above, to calculate $\Delta\beta$ and ΔC_p. It must be emphasized that the values so found are in many cases very inaccurate. I have, however, thought it worth while to give them, because this is a matter about which absolutely nothing seems to be known, and is obviously one of extreme importance for the understanding of polymorphic forms. In fact, even the sign of these quantities does not seem to be known at present; we do not know (except perhaps in a few cases) which of two polymorphic forms has the greater compressibility or thermal expansion or specific heat. The values given in the following would fully justify themselves if they should even give the sign correctly.

DATA.

The data for the individual substances follow.

POTASSIUM SULFOCYANIDE. This was Kahlbaum's purest, "zur Analyse," used without further purification. Two sets of readings were made; one consisted of five points on the transition curve and two on the melting curve at higher pressures, and the other was of one point on the transition curve at low pressures. The transition from one solid to the other is sharp, so that apparently the solid does not form mixed crystals with whatever impurity is present. There is some impurity present, however, as shown by a rounding of the corners of the melting curve, but it must be small in amount, because the melting and freezing ran unusually rapidly and approached closely the same values from above and below, nearly independently of the amount melted. The impurity is most probably a small amount of moisture. For the determination at low pressures the substance was carefully dried in vacuum for seven hours at 100°. The value for ΔV found here lies on a smooth curve with the values found at higher pressures, so the effect of the impurity must be very slight.

For the determination at high pressures, during which melting was to occur, the KSCN in the form of fine crystals was hammered compactly into a steel shell, open only at the top. For the determination at low pressures, without melting, the fine crystals were hammered into a steel shell open at both ends and perforated on the sides with numerous small drill holes. The somewhat greater restraint offered by the steel shell in the first run seemed to have no harmful effect. The quantity used was about 47.5 gm. Pressure was transmitted directly by kerosene.

The experimental results are shown in Figures 4 and 5 and the computed values of ΔH and ΔE in Figure 6. Table I gives numerical values at even pressure intervals. It is especially to be noticed that the values given for the melting curve are only approximate; since no great effort was made to get these very accurately. Only two points were determined, so the curvature can not be stated. The transformation curve and the ΔV curve for the transition solid-solid are both like the corresponding curves for liquids. The ΔH curve falls, however, whereas for the majority of liquids it rises.

The effect of pressure on the transition and melting does not seem to have been previously determined, so there are no values for compari-

son at high pressures. The transition point by extrapolation (the lowest point was 240 kgm.) from the present measurements is 140°, against 146° by Gossner.[4] The melting point extrapolates to 171.2°, against the values 161.2° by Pohl in 1851 (quoted in the French Tables), 173.8° by Wagner and Zerner,[5] and 174.2° by Wassiljew.[6]

TABLE I.

POTASSIUM SULFOCYANIDE.

Pressure	Temperature	ΔV cm³./gm.	$\dfrac{dt}{dp}$	Latent Heat kgm. m./gm.	Change of Energy kgm.m./gm.
			I–II.		
1	140°.0	0.00306	0.00954	1.325	1.325
500	149 .2	274	892	1.297	1.283
1000	157 .9	245	841	1.256	1.231
1500	166 .1	221	801	1.212	1.179
2000	173 .9	200	772	1.158	1.118
2500	181 .5	183	752	1.107	1.061
3000	189 .1	170	743	1.058	1.007
3500	196 .5	159	735	1.016	0.960
4000	208 .3	151	728	0.969	0.909
		LIQUID–I (Approximate values).			
1	171°.2	.0497	.0214	10.3	10.3
500	181 .9	480	"	10.2	10.0
1000	192 .6	463	"	10.1	9.6
1500	203 .3	446	"	10.0	9.3

It should be noticed that the extrapolated value of the melting point is probably too high, because no account is taken of the certain curvature of the melting curve. It is to be remarked that a high transition temperature is not presumably more correct than a low one, as it is in the case of melting. Impurity in the form of mixed crystals must be proved before such a presumption can be recognized, and even then,

4 B. Gossner, ZS. Kryst. **38**, 110–168 (1903).
5 K. L. Wagner and E. Zerner, Monatsh. Chem. **31**, 833–841 (1910).
6 H. Wassiljew, Chem. Centralbl. 1910, II, 56.

there is the possibility that the impurity is dissolved in the low temperature phase, contrary to the case for melting. Gossner gives the density at room temperature as 1.898. There seem to be no other values of ΔV or ΔH at atmospheric pressure.

No other modifications were found to 12000 kgm. at 20° or 160°.

The directly measured values of the difference of compressibility, which were self consistent, indicate an abnormally large difference between the two phases. The difference increases rapidly with increasing pressure and temperature, the low temperature phase being more compressible. But the measurements cannot be accurate, the values being much too large, because they lead to impossibly large
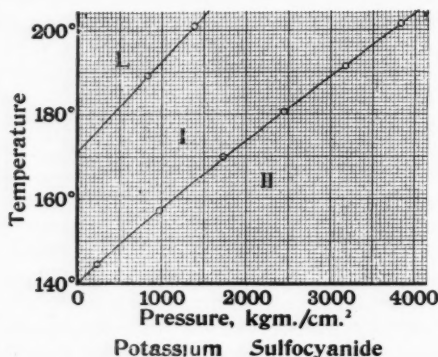

FIGURE 4. Potassium Sulfocyanide. The observed equilibrium pressures and temperatures.

differences of the specific heats. The direct measurements would indicate that the low temperature phase has the higher expansion and the higher specific heat. In addition to the measurements of the difference of compressibility, the difference of expansion was measured at low pressures (77 kgm.). This measurement is more moderate than the high pressure ones, but also demands that the low temperature form have the higher compressibility, expansion, and specific heat. The values at 77 kgm. are as follows;

$$
\left.
\begin{aligned}
\Delta\alpha &= -0.0_65 \\
\Delta\beta &= -0.0_312 \\
\Delta C_p &= -6.1 \text{ (kgm. cm.)}
\end{aligned}
\right\}
$$

The reason for the too high difference of compressibility found at high pressures is not clear.   At any rate, one would seem justified in assuming that KSCN is abnormal in that the low temperature form is more compressible, expansible, and has a higher specific heat than the high temperature form, and that the differences are unusually large.
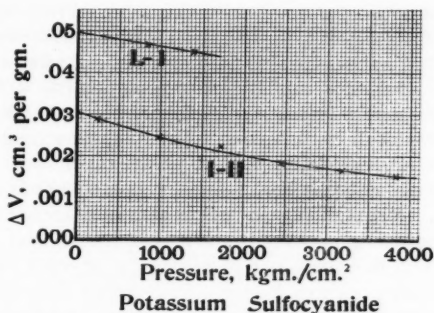

FIGURE 5.   Potassium Sulfocyanide.   The observed differences of volume between the liquid and solid I, and between solids I and II.
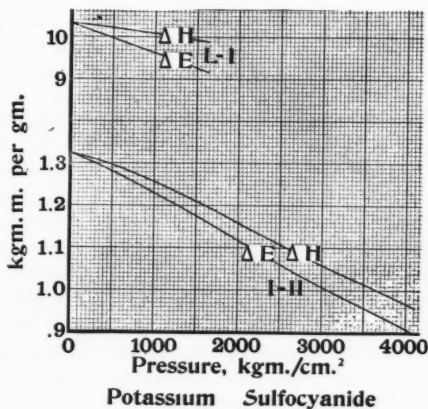

FIGURE 6.   Potassium Sulfocyanide.   The computed values of latent heat and the changes of internal energy.

NH₄SCN. This substance was Kahlbaum's purest, "zur Analyse," used without further purification, except heating to 100° for several hours in a vacuum, to remove all traces of moisture. Measurements were made with three different fillings of the apparatus. The first two were at the higher pressures, and for these the dry NH₄SCN powder was hammered into a compact mass in a steel shell, open at both ends and with perforations in the sides. Pressure was transmitted directly by kerosene. The third filling was for the run at low pressures, and for this the dry powder was hammered into the inverted nickel steel shell, and pressure transmitted to it by mercury. The difference in the pressure transmitting medium caused no perceptible difference in the behavior. The quantities used were about 34 gm. for the first two fillings, and 21 gm. for the third.

A transition point was first found at about 2200 kgm. at room temperature. NH₄SCN was known to be dimorphous, but the transition at atmospheric pressure is about 90°, so it seemed at first that there was here a third new modification. On determining the transition at other temperatures, however, it appeared that this was not a new form, but that the transition line runs from high to low temperatures with increasing pressure; that is, the high temperature form has the smaller volume. This somewhat unusual behavior does not seem to have been noticed; at any event this fact has not found its way to tables of crystalline properties, nor in Gossner,[4] who has published the most extensive investigation on this substance. Four points were found with the first filling of the apparatus, from 0° to 67°. The temperature was then raised to 200° in the search for other modifications. At about 4500 kgm., an irreversible change took place, with an increase of volume of about 0.04 cm³/gm. No other transition could be found on increasing pressure to 12000 kgm., and then no transition at all on releasing pressure from 12000, although the melting curve ought to have been crossed. On opening the apparatus, it was found that the irreversible transition was really a decomposition. Very little gas was given off by the decomposed products, but the smell was probably the worst that has ever been artificially produced. The solid products of the decomposition were of a bright yellow color, probably due to free sulfur, but no further analysis was attempted. The products of the decomposition found their way through the whole of the apparatus, and deposited themselves on the manganin coil, short circuiting it, so that it had to be thrown away. The second filling of the apparatus was made to redetermine one point at about 2200 kgm., the ΔV value for which did not fall on a smooth curve

with the other values.   For this determination, a new manganin coil
was used, which however, had been previously carefully seasoned.
Both the values of equilibrium pressure and temperature and ΔV found
with this coil lie on a smooth curve with the other points, bespeaking
the accuracy of the manganin coils.   Two points were determined
with the low pressure apparatus; one by the method of varying
temperature at a constant pressure of 77 kgm , and the second by
varying pressure at constant temperature, the equilibrium pressure
being about 240 kgm.   The values found at 77 kgm. did not agree
with the other values, and were discarded; the error is apparently
an effect of air in the apparatus, which of course becomes vanishingly
small at higher pressures.

The transition between the two solids runs cleanly and sharply,
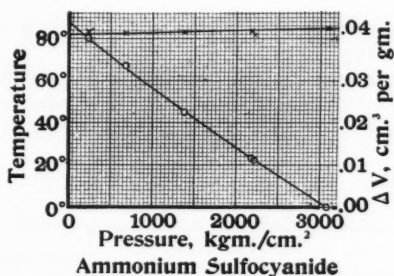very nearly the same pressure being reached from above and below.

FIGURE 7.   Ammonium Sulfocyanide.   The observed equilibrium tempera-
tures and pressures, and the changes of volume.

The change of volume of NH_4SCN was large enough so that it was
possible to measure the time rate of reaction, that is, the time rate of
recovery of pressure.   These results will be given in another paper.
The retardation effects, either superheating or subcooling, were not
large; no careful attempt to measure these was made.   It is probably
safe to say that the reaction ran invariably if the transition line was
crossed as much as 300 kgm. in either direction.

The experimental points are shown in Figure 7, the computed values
of ΔH and ΔE in Figure 8, and a summary of the numerical values is
given in Table II.   The exceptional curvature of the transition line
is to be noted.

There seem to be no previous determinations of the effect of pressure on the transition point, nor of the change of volume or the latent heat at atmospheric pressure. The previously listed value of the transition temperature is 92°, against 87.7° found by extrapolation. Gossner [4] also states that the transition is very sharp (as was found
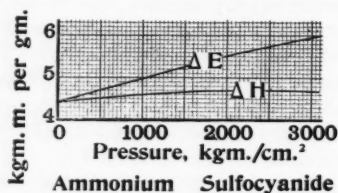

FIGURE 8. Ammonium Sulfocyanide. The computed values of the heats of transition and the changes of internal energy.

above), that the melting point is 169°, and the specific gravity 1.305 at room temperature.

Several fairly consistent measurements of the difference of compressibility of the two phases were made. The results are shown in

TABLE II.

AMMONIUM SULFOCYANIDE.

Pressure	Temperature	ΔV cm³./gm.	$\dfrac{dt}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
1	87°.7	0.0409	−0.03336	4.423	4.423
500	71 .5	412	3146	4.508	4.714
1000	56 .2	414	2976	4.581	4.995
1500	41 .7	417	2828	4.636	5.261
2000	27 .9	419	2698	4.675	5.513
2500	14 .7	422	2590	4.683	5.738
3000	2 .0	424	2494	4.677	5.949

Table III. The high temperature phase, that is, the phase with the smaller volume is less compressible, more expansible, and has the smaller specific heat. The differences between the two phases become smaller at the higher pressures. The sign of the difference of compressibility seems natural, but one might perhaps expect the high temperature phase to have the higher specific heat. It is remarkable that the behavior of the two phases here is the exact opposite of water and ice I. Water at low pressures is more compressible, less expansible, and has a higher specific heat than ice.

No other modifications were found to 12000 kgm. at 0°, or to 11000 at 100°. The decomposition at high temperatures prevented search for other modifications at higher temperatures, and also made it use-

TABLE III.

AMMONIUM SULFOCYANIDE.

Pressure	$\Delta\alpha$	$\Delta\beta$	ΔC_p
1	$-.0_5 49$	$+.0_3 17$	-3.6
1000	$-.0_6 42$	$.0_3 16$	-3.6
2000	$-.0_5 34$	$.0_5 14$	-3.5
3000	$-.0_5 27$	$.0_3 13$	-3.0

less to try for points on the melting curve. It is a little surprising that no other modifications were found. The abnormality of the high temperature modification, since it is formed with decrease of volume, might lead one to expect that at high pressures it would be replaced by another modification giving a phase diagram something like that of AgI. It may be, of course, that it is not the high temperature form that is abnormal, but that instead it is the low temperature form that has an abnormally large volume. In this case, the phase diagram is the natural one.

The possible relationship of the several modifications of KSCN and NH₄SCN is suggested by the crystalline forms. At first sight it is surprising to find different types of phase diagrams for these two substances, because K and NH_4 usually replace each other isomorphously. Gossner [4] has shown, however, by a comparison of the crystalline forms,

that the ordinary modifications of KSCN and NH₄SCN are not corresponding modifications. The low temperature form of NH₄SCN is monoclinic, and the high temperature form rhombic, whereas the low temperature form of KSCN is rhombic, and the high temperature form belongs to some other system of which all that can be said is that it is doubly refracting. The rhombic forms of the two substances are isomorphous, forming mixed crystals. If NH₄SCN and KSCN are really isotrimorphous we would expect another modification (not yet discovered) of KSCN at low temperature. Failure to find another form of NH₄SCN at high pressures is evidently because the lower transition is of the ice type. The absence of the upper transition line for NH₄SCN may be explained by supposing that the rhombic modification melts before the temperature can be raised to the transition value.

POTASSIUM SULFIDE. — This was Kahlbaum's purest, "zur Analyse," not further purified. Two runs were made; the first at higher pressures, and the second at 77 kgm. The quantity used was about 47 gm. For both runs the salt was hammered into an open steel shell with lateral perforations, and pressure was transmitted directly to it by kerosene. K_2S is exceedingly hygroscopic; it was necessary to work very rapidly in transferring it to the shell, and it was almost impossible to avoid the collection of some slight amount of moisture from the air.

It does not seem to have been previously noted that K_2S is dimorphic at atmospheric pressure. This is doubtless to be explained by the very slight change of volume (accompanied by a very small heat effect), and the inconvenience of making observations at atmospheric pressure because of the extreme hygroscopy. With the apparatus and the quantity used the discontinuity of the piston displacement was only 0.01 inches. Observation of the transition at low pressures is further rendered difficult by the fact that the transition point is fairly near the decomposition point at atmospheric pressure. At 77 kgm. effects were observed only 15° above the transition temperature which are probably to be explained by incipient decomposition.

The transition line must be passed by about 200 kgm. in either direction before the reaction runs. The change of volume is so slight that the pressure does not return to the equilibrium value after the reaction starts, but the reaction runs to completion with exhaustion of one phase, before the pressure can return to the equilibrium. This means that the equilibrium pressures are enclosed within considerably wider limits than is usually the case. The p–t points are, therefore,

more irregular than usual.   The same cause produces an even greater irregularity in the ΔV values; we have here a large percentage error due both to the extreme smallness of the change and the necessity for a considerably wider extrapolation than usual.   To reduce this error as much as possible, the measurements of ΔV were made with both increasing and decreasing pressure.

The very small change of the volume and the comparatively large lag of the reaction combine to make impossible measurements of the rate of the reaction.   After the reaction had once started, it ran to completion within the time required for the dissipation of the ordinary heat of compression.

The experimental results are shown in Figure 9, the computed values for ΔH and ΔE in Figure 10, and the numerical values in Table
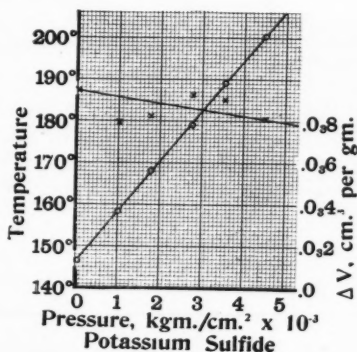

FIGURE 9.   Potassium Sulfide.   The observed equilibrium temperatures and pressures and the changes of volume.

IV.   The behavior of the various quantities is like that of a typical liquid.

There are no other values for comparison, since it was not known before that K_2S is dimorphic.

The direct measurements of the difference of compressibility are irregular and inaccurate, but the probability is that the low temperature form of K_2S is the more compressible, the difference of compressibility being of the order of 0.0_51.   This means that the low temperature form is also more expansible, and has the higher specific heat.   The difference of expansion is of the order of 0.0_48, and of the specific heats of the order of 3 kgm. cm. per gm.

No other modifications were found to 12300 kgm. at 20° or to 12000 at 200°.

POTASSIUM CHLORATE. — This substance was Kahlbaum's purest, used without further purification.   It was hammered into a compact
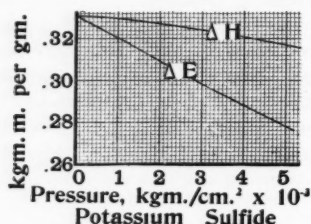

FIGURE 10.   Potassium Sulfide.   The computed values of the heat of transition and the change of internal energy.

mass in a thin steel shell, open at both ends, with lateral perforations, and the pressure was transmitted directly to it by kerosene.   53 gm. were used.   It is remarkable that it did not explode under pressure by spontaneous combination with the kerosene. $NaClO_3$ does so

TABLE IV.

POTASSIUM SULFIDE.

Pressure	Temperature	ΔV cm³./gm.	$\dfrac{dt}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
1	146°.4	.000948	.0120	.331	.331
1000	158 .4	918	"	.330	.321
2000	170 .4	886	"	.327	.309
3000	182 .4	855	"	.324	.298
4000	194 .4	825	"	.321	.288
5000	206 .4	794	"	.317	.278

explode; this will be described in detail later. Since the transition line of KClO$_3$ does not cross the axis of atmospheric pressure, one filling of the apparatus and one series of runs was sufficient to deter-mine all the data of the transition curve. A run with a second filling, pressure transmitted by mercury, was made to more carefully de-termine the velocity effects at 0°.

The reaction is a slow one, and shows considerable lag on both sides of the line. The pressure limits within which the equilibrium values were enclosed are wider than usual, the limits being very much widest at the low temperatures. The wide pressure limits at the low temperatures make the ΔV values rather irregular at the low end of the curve. The phenomena of reaction velocity are especially inter-esting and easy to follow in the case of this substance, and an especial study was made of them. These will be given in detail in another place. Attention may be called, however, to an experiment at 0° extending over four days. The equilibrium pressure found under these conditions is considerably higher than that to be extrapolated from the high temperature values.

The experimental results are shown in Figure 11, the computed value of ΔH and ΔE in Figure 12, and the numerical values in Table V. Within the limits of error, the transition line is straight, and the curve for ΔV is also straight, with a very small slope.

The new phase was not known before, so there are no other values for comparison.

No other forms were found be-tween atmospheric pressure and 12000 kgm. at room temperature, and none between 3000 and 12000 at 200°. There are, however, rea-sons for suspecting that there may

FIGURE 11. Potassium Chlorate. The observed equilibrium tempera-tures and pressures, and the changes of volume.

possibly be another modification at 0°, and that the transition line drawn should properly end in a triple point above 0°, with the line

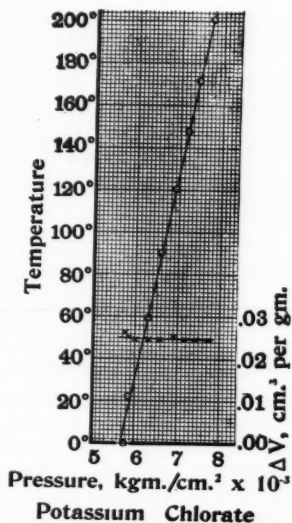branching below the triple point.   The reasons for this suspicion are
the high values of the equilibrium pressure found at 0° from the run
lasting four days, and also the high value found for ΔV at 0°.   The
high value of ΔV may be due to experimental error, which is larger
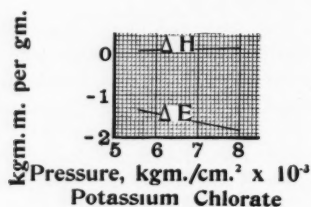than usual at 0° because of the great lag, but the high equilibrium

FIGURE 12.   Potassium Chlorate.   The computed heat of transition and
the change of internal energy.

pressure can hardly be explained in this way.   In any event, the
data given above for the lower end of the curve should be used only
with the greatest reserve; it seems that probably either the curve
should get steeper toward 0°, instead of remaining straight as drawn,
or else there is a new modification, and the transition line should
branch.

TABLE V.

POTASSIUM CHLORATE.

Pressure	Temperature	ΔV cm³./gm.	$\dfrac{dt}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
5680	0°	0.02510	0.976	.07026	−1.356
5880	20	2506	"	.07525	1.398
6090	40	2501	"	.08023	1.443
6290	60	2497	"	.08521	1.485
6500	80	2492	"	.09018	1.530
6700	100	2488	"	.09513	1.572
6910	120	2484	"	.1001	1.617
7110	140	2479	"	.1050	1.658
7320	160	2475	"	.1098	1.701
7520	180	2470	"	.1147	1.743
7730	200	2466	"	.1196	1.786

An attempt to find the crystalline form of $KClO_3$ II will be described in another place.

Seven measurements of the difference of compressibility between the two phases were made. These all point to the same conclusion; that the difference is very small, probably less than 0.0_62. This enables us to set upper and lower limits for the difference of expansion and specific heats. Assuming $\Delta\alpha = 0$, we find $\Delta\beta = -0.0_622$, and if $\Delta\alpha = 0.0_62$, $\Delta\beta = -0.0_715$. A value for $\Delta\alpha$ only 10 % higher than 0.0_220 would give a positive instead of a negative value for $\Delta\beta$. We conclude that the difference of thermal expansion between the two phases is unusually small, and that possibly, although not certainly, the high pressure phase is the more expansible. $\Delta\alpha$ and $\Delta\beta$ are so small that the values of ΔC_p are not affected by changes within the limits of error. ΔC_p is nearly constant over the entire range at -0.024 ($= -0.00056$ gm. cal. per gm.). Here again is a case where the phase stable at the lower temperature has the higher specific heat.

POTASSIUM NITRITE.—This substance was Kahlbaum's purest, used without further purification, except drying. After the runs had been made the irregularity of the results led me to take up the question of the purity of the substance with the J. T. Baker Chemical Co., and I learned from them that it is impossible to prepare KNO_2 pure commercially. There is always impurity of water and KNO_3. The impurity may be fairly large in amount, varying from 10 to 15%. An analyzed sample from the J. T. Baker Chemical Co. contained 89% KNO_2. The amount of water was not stated. These results, therefore, must be taken as merely indicating the order of the effects which may be expected with pure KNO_2. It is unfortunate that there was this large amount of impurity, because the results are interesting both because of the direction of curvature of the transition line, and the behavior of the reaction velocity.

Three fillings of the apparatus were used. With the first, only one point was determined, at 22°. The salt was not dried for this run, and considerable rounding of the corners led to the suspicion that moisture was present. For the second filling of the apparatus, the salt was dried in vacuum over H_2SO_4 for two days. Five points were found with this filling. For the third filling, the salt was dried in vacuum at 100° for several hours; three points were found with this filling. The different methods of getting rid of the moisture seemed to make no difference; the three runs were in essential agreement. In all three fillings the KNO_2 was hammered into a compact mass; the first two

runs were made with the pressure transmitted directly by kerosene, while for the third run, the compacted mass was submerged under mercury, by which the pressure was transmitted to it. Probably none of the attempts to remove the moisture was entirely successful; the KNO_2 was always different in texture from any of the other substances. When hammered, it compacted into a coherent semitranslucent mass, in texture like celluloid when cut with a knife.

The pressure limits within which the equilibrium was shut varied from 40 to 360 kgm.; in general the limits were wider at the lower temperatures, but the variations were very irregular. The irregularity is partly mixed up with the varying quantity of impurity at different stages of the reaction. The ΔV isothermal curves showed the effect of impurity by being rounded at the corners. The rounding took place

FIGURE 13. Potassium Nitrite. The observed equilibrium pressures and temperatures and the changes of volume.

at both corners; this is very unusual, and is the only case of it that I have found. It means that both of the phases form mixed crystals with the impurities, and that the impurity which is miscible with one phase is different from that miscible with the other. As one would expect from the rounding of both corners, no lag of the reaction was noticed in either direction from the transition line, at least beyond the region of indifference.

Beside the unusual rounding of both corners of the isothermals, KNO_2 is unique in that the reaction velocity is greater with rising

pressure than with falling. This was found at all temperatures; it may well be that it is not a genuine effect peculiar to the pure substance, but is connected with the separating out of mixed crystals of impurities.

The experimental results are shown in Figure 13, the computed

FIGURE 14.   Potassium Nitrite.   The computed values of the heat of transition and the change of internal energy.

TABLE VI.

POTASSIUM NITRITE.

Pressure	Temperature	ΔV cm³./gm.	$\dfrac{dt}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
5000	−3°.0	.0312	.0169	4.99	3.43
6000	14 .0	327	171	5.49	3.53
7000	31 .4	341	182	5.71	3.32
8000	50 .8	355	212	5.42	2.58
9000	74 .4	369	274	4.68	1.36
9500	89 .4	376	343	3.97	.40
10000	109 .3	383	472	3.10	− .73

values of ΔH and ΔE in Figure 14, and the numerical values in Table VI. The marked upward concavity of the transition line is unusual.

There are no other results for comparison. The data are too inaccurate to justify any attempts to estimate $\Delta\alpha$, $\Delta\beta$, or ΔC_p.

No new form was found to 12000 at 30° or 60°.

CARBON TRICHLORIDE.— This was Kahlbaum's purest, used without further purification. The powder was hammered cold into an inverted steel shell, and the pressure transmitted to it by mercury. Four fillings of the apparatus were made, two for the points at high pressures, and two for the points at low pressures (80 to 400 kgm.) About 21.5 gm. were used for the high pressure determinations, and 33 gm. for the low pressures.

C_2Cl_6 is known to have three modifications at atmospheric pressure, and hence two transition lines. These have already been investigated by Tammann [7] up to 3000 kgm. The substance promised to be an interesting one, because the transition lines diverge at atmospheric pressure, a phenomenon not shown by any other substance of which I know. It was of interest to see whether these lines would tend to come together again at high pressures. It is unfortunate, however, that this question could not be answered, because at the higher pressures on the transition line above 3000 kgm. the substance decomposes. The first run gave four points on the II–III curve to 177°. The transition runs cleanly on this line with no perceptible rounding of the corners. There is, however, some lag on both sides of the line. This lag, combined with the small change of volume, once or twice resulted in the pressure limits from above and below being as wide as 200 kgm., one phase being all exhausted before pressure could be restored to the equilibrium value. The lag at other points was not so great, and the pressure range was only 40 to 60 kgm. wide. The effects were very different on the I–II curve. The first point attempted on this curve was at 177°. Above the proper value of the transition pressure, the pressure began to rise slowly with time, just as it does with premature melting due to impurity. In the supposition that the effect was really due to impurity, the work was hastened so as to minimize as far as possible the effect. On arriving at the transition point, however, the rise of pressure continued at a nearly constant rate to nearly 1200 kgm. beyond the supposed point. On increasing pressure again, the automatic rise of pressure continued

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[7] G. Tammann, "Kristallisieren und Schmelzen," 298.

up to 3000 kgm. beyond the supposed transition point, that is to 6000 kgm. But above 6000 kgm. the secondary pressure reaction was a decrease after every increase. 6000 kgm. is above the II–III line, but no trace of this transition was found on crossing the line. On relieving pressure to 3500 the rise of pressure continued. On taking the apparatus apart, the C_2Cl_6 was found to have decomposed, and a good deal of mercury had disappeared. A suffocating gas was evolved, probably chlorine. There was, however, no apparent effect on the steel cylinders. This decomposition is an interesting one. It evidently was produced by the high temperature and not by the high pressure, for the reaction runs with increase of volume. The effect of pressure would be to prevent the decomposition; this is what occurred at 6000 kgm. Neither did the decomposition occur at the higher pressures of the II–III curve at 177°. The products of the decomposition found their way to all parts of the apparatus, which had to be taken apart and cleaned. The manganin coil had to be carefully cleaned, but recovered its normal resistance. With the second setting up of the apparatus, one point was found on the lower end of the II–III curve, and the other points were found on the I–II curve, not rising to the temperature of the previous decomposition. The order of points on the I–II curve was 102°, 136°, 86°, 104° and 120°. The first three of these determinations gave consistent values for pressure and temperature, and the second and third apparently gave good values for ΔV. The first point at 102° gave a value for ΔV impossibly low, as low as the II–III curve. This possibly was due to the transition not having been complete. The fourth and fifth points gave values of the pressures considerably lower than the other points and too high values for ΔV; evidently the decomposition had begun and was progressing. The decomposition had probably started at 136°, the highest temperature to which the material had been subjected, and then proceeded at an accelerated rate.

The points at low pressures were determined six months after those at high pressures. Six determinations were made, both at constant temperature and constant pressure. There were difficulties here also. At 77 kgm. there was evidence of decomposition at 90°. This may have begun earlier; the ΔV value of this attempt was not good. The other attempts by the method of varying pressure at constant temperature gave good results on the I–II curve, but ΔV on the II–III curve was lower than to be expected from the high pressure points. This might be due in large measure to the extreme slowness of the reaction from below on the II–III curve. Working at low pressures, the pres-

sure could not be released far enough to ensure the completion of the
reaction, and hence the ΔV values were too low.

We see that the results are affected by numerous irregularities, due
to unavoidable decomposition at the high temperatures, and the slow-
ness of the reaction at the low temperatures and pressures.   But on
the II–III curve the points all lie regularly, as do also the ΔV points at
high pressures.   Satisfactory values for ΔV at low pressures could not
be obtained, and the value listed for atmospheric pressure was obtained
by extrapolation of the high pressure values.   It is to be noticed
that the II–III curve shows increasing curvature at the high pressures.
This is unusual; it may possibly be the effect of impurities, although
the regularity of the ΔV points would seem to preclude this.   On the
I–II curve, the p–t values at high pressures are irregular because of
decomposition, and only one good value of ΔV was found at high
pressure.   The values both for p, t and ΔV at low pressures are, how-
ever, apparently satisfactory for I–II.   To obtain better values would
require a great multiplication of experiments.   It might be worth
trying water as the transmitting medium, as possibly the action of
mercury is such as to start the decomposition.   In any event, it would
probably not be possible to greatly exceed the temperature reached
here without decomposition, and the interesting question as to whether
the lines I–II and II–III ultimately approach each other would remain
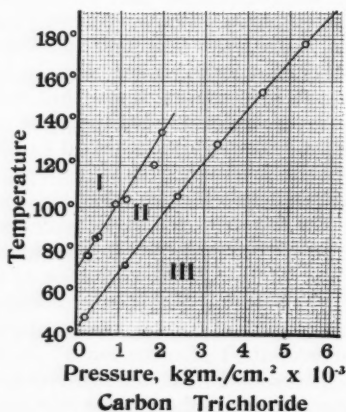unanswered.

FIGURE 15.   Carbon Trichloride.   The observed equilibrium temperatures
and pressures.

The experimental results are shown in Figures 15 and 16, the computed values of ΔH and ΔE in Figure 17, and the numerical values in Table VII.   All the determinations of the p–t points are shown in the

FIGURE 16.   Carbon Trichloride.   The observed differences of volume between the several phases.
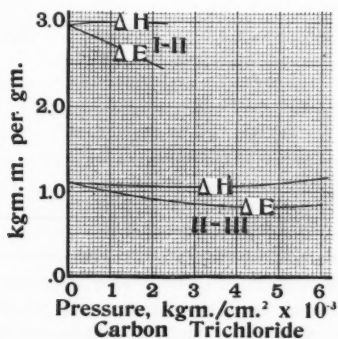

FIGURE 17.   Carbon Trichloride.   The computed values of the heats of transition and the changes of internal energy.

figures, but the bad values of ΔV are omitted, as these are much more subject to error; in fact, one of the ΔV points falls on the wrong curve.

No other modification was found to 12000 kgm. at room temperature.

There are a few values for comparison. For the transition point, Schwarz [8] found by an optical method that the II–III transition was between 43.1° and 46.6° and the I–II point at 71.1°. The value found above for the II–III transition was 42.7°, by extrapolation. I have adopted the value of Schwarz for the I–II point, because of the irregularity of my points. The transition line was drawn as the best straight

TABLE VII.

CARBON TRICHLORIDE [C_2Cl_6].

Pressure	Temperature	Δv cm³./gm.	$\dfrac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
		II–III.			
1	42°.7	.0097	.0273	1.122	1.122
1000	69 .8	85	268	1.087	1.002
2000	96 .3	75	260	1.065	.915
3000	121 .9	67	250	1.059	.858
4000	146 .3	61	238	1.073	.829
5000	169 .5	56	225	1.102	.822
6000	191 .3	52	208	1.161	.849
		I–II.			
1	71°.1	.0280	.0326	2.96	2.96
1000	103 .7	259	"	2.99	2.73
2000	136 .3	238	"	2.99	2.51

line from Schwarz's point to the high pressure points. If, however, it had not been for Schwarz's value, and if only the lowest points of the I–II curve had been used, as most probably unaffected by impurities, the I–II line would have shown distinct concavity toward the pressure axis, and the extrapolated transition point at atmospheric pressure would have been about 69°. Tammann [7] has determined the effect of pressure on the transition up to about 2000 kgm. He does not mention finding decomposition, but his highest temperature was

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8 W. Schwarz, Diss. Gött. (1892); Beibl. 17, 629–639 (1893).

only 130°. Both his transition lines are straight. His II–III transition point at atmospheric pressure is 41.8° and his II–III line lies at pressures from 30 to 50 kgm. higher than mine. The agreement in both these cases is better than is usual between his results and mine. On the I–II line, his atmospheric transition point is at 67.3°, and at 130°, his transition line is about 30 kgm. higher than mine. There are apparently no other determinations of ΔV or the latent heat at atmospheric pressure, and Tammann gives no values at high pressures.

Four measurements of the difference of compressibility between II and III were made. There can be no doubt that III is less compressible, but there may be considerable question as to the numerical value of the difference. On account of the decomposition between I and II,

<div align="center">

TABLE VIII.

CARBON TRICHLORIDE.

Differences between II and III.

</div>

Pressure	$\Delta\alpha$	$\Delta\beta$	ΔC_p
1	$+0.0_2 24$	$+.0_4 38$	$-.073$
2000	$.0_5 204$	$.0_4 41$	$+.23$
4000	$.0_5 174$	$.0_4 50$	$.70$
6000	$.0_5 146$	$.0_4 52$	1.25

no good values for the difference of compressibility between these forms could be obtained. The values of $\Delta\beta$ and ΔC_p computed from the experimental values of $\Delta\alpha$ are shown in Table VIII. The numerical accuracy is probably great enough so that one may say without question that II is more expansible; it is however, questionable whether the difference of expansion increases with rising pressure as the table shows. On the average, the specific heat of II is also greater than that of III; one may well doubt whether the difference is negative at atmospheric pressure as the table would show.

The crystalline forms of the several modifications has been determined by Lehmann.[9] The high temperature form is regular, the

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9 O. Lehmann, ZS. Kryst. 6, 580–589 (1882).

intermediate one asymmetric, and the low temperature modification rhombic.

CARBON TETRABROMIDE.— This substance is not carried in stock by any of the large chemical houses, but was made to order by Hoffmann and Kropff, and guaranteed by them to be chemically pure. Two separate lots were made by them, of about 100 gm. each. The second lot was perhaps purified more carefully than the first, being "triply distilled with steam," and showed a somewhat higher transition point. The particular interest of this substance lies in its suspected polymorphic isomorphism with CCl_4. In the first paper of this series two new modifications of CCl_4 at high pressures were found, and since the writing of that paper, I have learned that a transition point at atmospheric pressure, on the prolongation of the transition line at high pressures, has been discovered by Goldschmidt [10] at $-47°$. Now it is known that CBr_4 is dimorphic at atmospheric pressure, the transition being at about 47°. The suspicion was strongly suggested that the transition point of CBr_4 at 47° corresponds to the newly found one of CCl_4 at $-47°$, and that at high pressures another modification of CBr_4 would be found corresponding to the third modification of CCl_4. As a matter of fact, another modification was found, but it does not have at all the relation to the other two forms that is suggested by CCl_4. It is unfortunate that here, as in the case of C_2Cl_6, the substance begins to decompose just where things are getting most interesting.

Measurements were made with five different fillings of the apparatus. With the first lot, two sets of readings at high pressures were made; one at 200°, which was terminated by decomposition, and the other to only 100°. A third filling with this lot was made for the low pressure point. With the second lot, one filling was made for high pressure measurements to 123°, and one filling for the low pressure point. The quantity used varied from 35 to 59 gm. In all cases the substance was hammered cold into the inverted steel shell, and pressure transmitted to it by mercury.

These several runs are perhaps worth describing in some detail, both because the new modification belongs to a new type, and because of the decomposition effects, which are interesting in themselves, and which might without detailed description, be thought to make questionable the validity of the new transition. It was of course expected,

10 V. M. Goldschmidt, ZS. Kryst. **51**, 26 (1912).

in analogy with CCl_4, that a new modification would be found on increasing pressure at room temperature. None was found, however, up to 12000 kgm. Temperature was then raised to 127°, and pressure relieved from 12000. Two transitions were found, at 2800 and 2310. These transitions both ran sharply, with no rounding of the corners, and were entirely reversible. The change of volume at the lower transition was considerably less than that of the higher. Even the approximate location of the melting curve was not known at the time of this run, so that the low pressure transition might have been melting, although this seemed unlikely in view of the complete absence of rounding of the corners. Temperature was then raised to 152°, and the transitions found with decreasing pressure. Two transitions were found, but separated by a much wider interval than before, and there was some preliminary rounding of the corner at the lower point. This lower point might have been melting this time, therefore, but there seemed no connection with the low point at 127°. Temperature was now raised to 176°. The regular transition was found at high pressures, on a line with the other two points, and a lower point was also found. This lower point was too high to fall with either of the other two lower points, and the transition was partly reversible and partly irreversible; that is, on increasing pressure the return of volume to the original value was not complete. At 176°, pressure was now raised to 6000, and the temperature raised to 200°. Pressure was now increased to 12000 kgm. Two notable decreases of volume were found on the way to 12000, at approximately 6800 and 7500. But on decreasing pressure, no transition of any kind could be found down to 4000 kgm., that is, considerably beyond the higher of the two transition lines. The apparatus was now cooled and taken apart; the CBr_4 was found completely decomposed into carbon and bromine. The products of the decomposition reached all parts of the apparatus, and there was considerable trouble in cleaning it. In view of this decomposition and of the fact that the higher of the transition points lie on a line which extrapolates with little curvature to the known transition point at atmospheric pressure, this first run was supposed to indicate only one modification, the lower transition points being ascribed to some obscure effect of the decomposition.

With this conclusion, the subject was dropped for over a month, when the rest of the first lot of material was used in the low pressure apparatus to fix the transition data at atmospheric pressure. Two runs were made with this; one with increasing temperature at constant pressure, and the other with decreasing pressure at constant

temperature. The corners of the curves were rounded, an effect not found before at high pressures. Evidently the CBr$_4$ had become impure on standing. This same lot of CBr$_4$ was then used again in the high pressure apparatus to give two points on the transition line below 127°, the lowest temperature previously used. The data were apparently all in; but on working them up, it appeared almost unmistakable that the two low pressure transition points first found were genuine, really belonging to a new modification, and were not the effect of decomposition. The evidence which made this almost inescapable was the values of ΔV, which had not been computed before. There was a discontinuity in the values for ΔV along the transition line, the amount of discontinuity corresponding very closely with the ΔV found for the questionable points. Furthermore, the points on the lower end of the transition line, below 127°, did not lie smoothly with those above 127°, but there was a pronounced change of direction at about 110°. The perfect reversibility of the two suspected transitions strengthened the probability. The reason why it took me so long to admit that this was a new form, was because thus is a new type of transition, in which a new form appears at high pressures and temperatures with a volume intermediate between the two low pressure forms; there seems to be no excuse for the existence of such a form. In order to make certain that there was really a new form, a fresh lot of CBr$_4$ was ordered from Hoffmann and Kropff, with the request that they take special precautions in purifying it. This lot was triply distilled in steam. The new material was first used in the high pressure apparatus. The first point was obtained at 108°, below the supposed triple point, and the second at 123°, above the supposed point and as near to it as was convenient to work. Only one transition was found at 108°, but two at 123°. The lower of these two, which is the questioned one, was found to be reversible exactly as before. There could be no doubt of the genuineness of the transition. It is unfortunate that this second lot decomposed at a lower temperature than the first lot; the decomposition was barely perceptible as low as 108°, and at 145° was proceeding so rapidly that even p–t values for the higher pressure could not be obtained. The ΔV values at 108° and 123° with this second lot are both too high because of decomposition. The rest of this second lot was used for a determination of the transition point at low pressures by the method of changing pressure at constant temperature: The value found by extrapolation for the transition temperature was 46.2°. This is somewhat higher than the value given by the first lot, and as there was less rounding of the cor-

ners, this sample is evidently purer, although it was not perfectly pure, because there was perceptible rounding for this also.   The agreement of the two samples at high pressures is better than at atmospheric pressure; doubtless considerable of the impurity shown by the first sample at low pressures was due to a gradual decomposition, and did not affect the values at high pressures, which were determined nearer to the time of preparation of the sample.

The decomposition phenomena are of special interest; apparently there are two kinds of decomposition.   The first sample showed both kinds.   The first kind of decomposition is one with increasing volume and took place in notable degree for the first sample at 176°.   This is evidently an effect of the high temperature, and not of the pressure. The second decomposition is one with decreasing volume, and was shown by the first sample at 200° and about 7000 kgm.   Because of the decreasing volume, we can tell that this is probably a decomposition brought about by the high pressure and not by the high temperature. Such decompositions are not usual; this is the first case of it I have found.   Apparently the result of this decomposition with decreasing volume is complete resolution into carbon and chlorine.   The second sample showed only the first kind of decomposition with increasing volume at 145°; at this temperature the decomposition ran very nearly to completion, only a small trace of the II–III transition being found on decreasing pressure.   The apparatus was cooled and taken apart after the decomposition at 146°.   There was some free bromine, but apparently no free carbon.   The larger part of the mass was a white solid, but several cu. cm. of a colorless liquid had been formed. After this run, the steel shell with the CBr_4 was sealed into a glass tube to preserve the decomposition products.   The colorless liquid was unstable; after several weeks it had entirely disappeared, its place being taken by hexagonal crystalline plates.   This is not the crystalline form of either of the forms of CBr_4.   The chemistry of this decomposition might prove an interesting subject for investigation.

As regards the accuracy of the results given above, the p–t values are probably pretty good, but the ΔV values are too high on the I–III and the II–III curves.   This is the result of the slow decomposition, even at low temperatures.   It is known that at atmospheric pressure CBr_4 decomposes at 100°, so that the decomposition found here is not surprising.   As a result of the high ΔV values, the ΔH values are also at fault.   There can be no question of this, because they do not check at the triple point.   There seemed to be no way of adjusting the various

quantities easily so that the ΔH values should check, and the values of the tables are left with this error. This is the only substance for which the values have not been so adjusted as to check at the triple point. In the case of other substances the amount of necessary adjustment is so slight and is indicated so unambiguously, that the probable accuracy of the individual curves can only be increased by demanding that the necessary conditions at the triple point be accurately satisfied; but here the error is great enough so that the precise direction in which the adjustment should be made is not indicated unambiguously and hence the adjusted values would be likely to have as much or more error than the unadjusted ones. The amount of adjustment is not so very large even here; an increase of one value of ΔH by 3.5 % and a decrease of another by the same amount would satisfy the conditions.

The experimental results are shown in Figures 18 and 19, the computed values of ΔH and ΔE in Figure 20, and the numerical values are collected in Table IX. In the figures the values of ΔV are not given which are obviously in error because of decomposition. In the phase diagram the initial direction of the melting curve is indicated. This is taken from the work of Wahl, who found that because of decomposition, the melting curve could be followed only about 10° above the normal melting point. The initial slope of the melting curve is unusually high; in this work no attempt was made to obtain any of the data of the melting curve.

Other results for comparison are as follows. For the transition point at atmospheric pressure Schwarz [8] gives 46.1° by an optical method, and Rothmond [11] gives 46.91° by a thermometric method. Wahl [12] seems to have been the only previous experimenter on the effects of pressure. His transition curve extrapolates to 47.3° as the transition point at 1 kgm. The extrapolated value found above from the second purer lot was 46.2°. The specimens of Rothmund and Wahl were, therefore, probably purer than those used above; in particular, Wahl's specimen seems to have been purified with very great care. Wahl also followed the transition line I–II up to 1500 kgm. At 1500 his transition temperature is 2.8° higher than mine, whereas it starts 1.1° higher at atmospheric pressure. The difference of slope, which amounts to about 3.5%, may be an effect of impurity. One point investigated with especial care by Wahl was that of the

11 V. Rothmund, ZS. phys. Chem. **24**, 705–720 (1897).
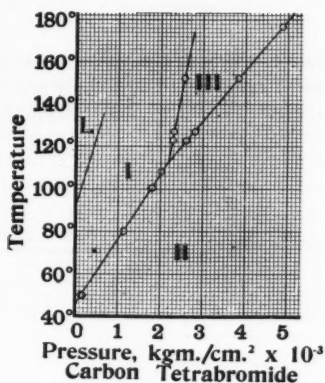12 W. Wahl, Trans. Roy. Soc. **212**, 117–148 (1912).

FIGURE 18. Carbon Tetrabromide. The observed equilibrium temperatures and pressures.
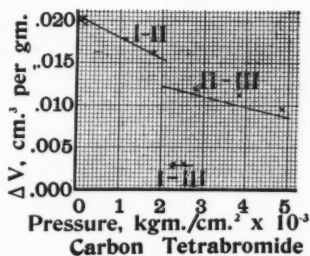

FIGURE 19. Carbon Tetrabromide. The observed differences of volume between the several phases.
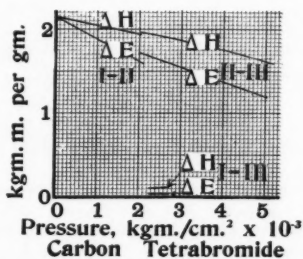

FIGURE 20. Carbon Tetrabromide. The computed values of the heats of transition and the changes of internal energy.

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breadth of the band of indifference between the two phases.   He found
it to vary from 30 to 55 kgm., not showing any regular dependence on
pressure or temperature.   The breadth of the band found by me above

TABLE IX.

CARBON TETRABROMIDE.

Pressure	Temperature	ΔV cm³./gm.	$\dfrac{dt}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
			I–II.		
1	46°.2	.0205	.0305	2.15	2.15
500	61 .4	192	"	2.10	2.00
1000	76 .7	179	"	2.05	1.87
1500	91 .9	167	"	2.00	1.75
2000	107 .2	155	"	1.93	1.62
			I–III.		
2250	119°.5	.0029	.1054	.108	.044
2500	145 .8	29	"	.115	.043
2750	172 .2	29	"	.123	.043
			II–III.		
2000	108°.5	.0123	.0238	1.97	1.72
3000	132 .3	110	"	1.87	1.54
4000	156 .1	097	"	1.75	1.36
5000	179 .9	085	"	1.62	1.19
			TRIPLE POINT.		
2180	112°.6				

varied from 43 to 58 kgm. at the higher pressures, essentially the same
as that found by Wahl.   At 100 kgm., however, lower than any of the
measurements of Wahl, the band was only 11 kgm. wide.   Rothmund

has also remarked on the sharpness of the transition at atmospheric pressure. The essential agreement of Wahl's and my results at high pressures for the width of the band of indifference, by methods entirely different, would seem to indicate some real physical significance in the absolute values found by us, characteristic of the substance, and not a property of the particular form of apparatus. The width of the II–III band was distinctly greater than that of the I–II band, being from 70 to 100 kgm., while that of the I–III band was less, 11 to 33 kgm. There seem to be no previous determinations of either ΔV or ΔH for the transition.

The data do not justify any attempt at estimating $\Delta\alpha$, $\Delta\beta$, or ΔC_p.

SILVER IODIDE.— This substance was Eimer and Amend's purest, used without further purification. Only one filling of the apparatus was necessary in getting the high pressure points, and one for the low
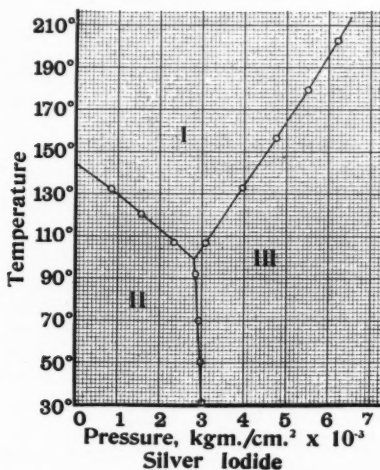

FIGURE 21. Silver Iodide. The observed equilibrium temperatures and pressures.

pressure points. The transitions ran cleanly, and gave no such trouble from lag as was found by Tammann.[13] The dry powder was

13 G. Tammann, "K. und S," p. 302, and ZS. f. Phys. Chem. **75**, 733–762 (1911).

BRIDGMAN.

compressed by ramming into an open steel shell, and pressure trans-
mitted directly to it by kerosene. Apparently there was no soluble
impurity present, because no rounding of the corners of the isothermals
was ever detected. The quantities used were 85 and 103 gm.

FIGURE 22. Silver Iodide. The observed differences of volume between
the several phases.

FIGURE 23. Silver Iodide. The computed values of the heats of transition
and the changes of internal energy.

The width of the band of indifference was not nearly so great for
this substance as was expected. It was greatest on the I–II curve,
being here nearly constant at 80 kgm., least on the I–III curve, where
it varied from 16 to 25, and intermediate on the II–III curve, where it
varied from 20 to 60, being greatest at the lowest pressures. The

TABLE X.

Silver Iodide.

Pressure	Temperature	ΔV cm³./gm.	$\dfrac{dt}{dp}$	Latent Heat kgm.m./gm	Change of Energy kgm.m./gm.
		I–II.			
1	144°.6	.00860	− .0146	2.460	2.460
1000	129 .6	914	155	2.374	2.465
2000	113 .5	964	167	2.232	2.425
3000	96 .1	1020	182	2.067	2.371
		I–III.			
3000	104°.8	.01390	.02904	1.808	1.391
4000	134 .0	1286	2947	1.776	1.262
5000	163 .9	1130	3060	1.614	1.049
6000	195 .4	0936	3260	1.339	.777
6500	212 .3	0830	34 −	1.188	.649
		II–III.			
3000	30°.0	.0239	− .415	.175	.892
2951	50 .0	2395	.390	.198	.905
2897	70 .0	240	.347	.237	.932
2835	90 .0	2408	.297	.294	.976
2800	100 .0	2412	.273	.329	1.005
		Triple Point.			
2810	99°.4	I–II .01010	− .01787	2.105	2.39
		I–III .01402	.0290	1.801	1.41
		II–III .02412	− .276	.325	1.00

reactions on all three curves were fairly rapid. The total time required to shut the pressure within the limits above, both from above and below, averaged about 20 minutes on the I–III curve, one hour on the I–II curve, and 20 minutes on the II–III curve, except at 30°, which required 50 minutes. In no case was much lag observed in going across any transition line in either direction. No careful measurements of this were made; at 107° the reaction from III to I ran on crossing the transition line by only 45 kgm.

The experimental results are shown in Figures 21 and 22, the computed values of ΔH and ΔE in Figure 23, and the numerical results in Table X. None of the experimental points have been discarded. It should be noticed that although in the table ΔV is given as increasing with increasing temperature on the II–III line, the increase is slight, and perhaps within the limits of error. No theoretical deductions should be based on this increase of ΔV. A notable feature of the phase diagram is the downward convexity of the I–III curve; such curvature is never shown by a melting curve, but there are several other examples of it for a solid transition.

There are several previous determinations of the constants of the transition. For the temperature of transition there is 145° by Kohlrausch [14] by an electrical method, 142° by Rodwell [15] from the discontinuity in length, Schwarz [8] gives 146.9° on heating and 145.4° on cooling, by the sudden change of color, Bellati and Romanese [16] give the transition point as approximately 150°, Mallard and Le Chatelier [17] as 146°, and Steger [18] 147°. Tammann [13] extrapolates to 144.2° from his measurements at higher pressures. The extrapolated value from the above work is 144.6°. For the latent heat of transformation Mallard and LeChatelier give 6.8 cal. and Bellati and Romanese 6.25 cal. at 150° against 5.77 cal. (2.46 kgm. cm.) found by calculation from Clapeyron's equation above. There seem to be no direct measurements of the change of volume of the transition at atmospheric pressure except the value 0.0028 cm³ per gm. which I have deduced with rather questionable assumptions from data of Rodwell.

The effect of pressure on the transition point was first investigated by Mallard and Le Chatelier, and has later been made the subject

14 W. Kohlrausch, Wied. Ann. 17, 642 (1882).
15 G. F. Rodwell, Proc. Roy. Soc. 25, 280–291 (1876–77), and Trans. Roy. Soc. 173, 1125–1168 (1882).
16 M. Bellati and R. Romanese, R. Inst. Ven. 1, 1043–1069 (1882–83).
17 E. Mallard and H. Le Chatelier, C. R. 97, 102–105 (1883).
18 A. Steger, ZS. phys. Chem. 43, 595–628 (1903).

of two papers by Tammann.   Reference is made to Tammann's paper for a historical account of our knowledge of the relation of the two phases.   It is to be noticed that my notation is different from that of Tammann.   I have employed consistently the numeral I for the high temperature form, whereas here Tammann applies it to the low temperature form.   The special interest in the pressure effects on this substance is because the forms I and II are of the rather unusual ice type, the form at the higher temperature having the smaller volume. Mallard and Le Chatelier found at 20° and 2475 kgm. a large decrease of volume; one would not expect a transition here from the initial trend of the curve at 1 kgm.   This led Tammann to take up the question, and he showed in his first paper that the effects were doubtless due to a third modification.   He was not able to obtain any very great amount of information as to this third modification, however, because of the large amount of lag which the reaction showed.   He took up the matter again later, however, and was able to get much better numerical results.   The data of the later paper of Tammann cover about the same range as the present paper as far as the I–II and the II–III curves go.   Tammann, however, followed the II–III curve carefully to a temperature 10° lower than that used here, and made measurements connected with the subcooling, etc., down to the temperature of liquid air.   The only extension of range in this paper is on the I–III curve, which is followed here to 200°, whereas Tammann did not determine accurately any points on it, but showed only that its slope was positive, and calculated its probable value.   Tammann in his second paper devoted a good deal of attention to the question of lag.   He found that at 90° the equilibrium pressure could be shut between the limits 2956 and 2957 kgm.; at 60° the limits were 2980 and 3040, and at 18°, 2760 and 3026.   The limits within which spontaneous formation of the nuclei took place were considerably wider than this.   In these experiments, on the other hand, the effect of lag was found to be much less.   As already stated, the greatest width of the band of indifference of the II–III curve is 60 kgm. at 30°.   The reason for this difference between our two experiments is not clear; possibly the kerosene had a catalyzing effect on the reaction which the heavy oil used by Tammann did not have, or it may be that this was in some way an effect of the much higher pressure to which the AgI was subjected in these experiments.   Before any readings had been taken, the AgI had been subjected to 12000 kgm. at room temperature. It is to be noticed, however, that Tammann in his first set of experiments reported in "Kristallisieren und Schmelzen" found a much

greater lag than he did in his later experiments. He was not able to repeat the early experiments, and was able to explain them only by supposing that the particular specimen of machine oil which he had used to transmit pressure had some peculiar property which the later specimens did not have.

A comparison of the numerical values of Tammann's later paper and the values found above gives the following results. Tammann found the change of volume I–II between 1000 kgm. and the triple point to be constant within the limits of error at 0.0095, the probable error being 5%. I found above that ΔV increases on the transition line from 0.0086 at atmospheric pressure to 0.00102 at 3000. Tammann's triple point is 2940 kgm. and 100°, against 2810 and 99.4° above. Tammann found the I–II line straight within the limits of error, with a slope of 0.01473; I found the slope to increase in absolute value from 0.0146 at 1 kgm. to 0.0182 at 3000 kgm. Tammann calculates the slope of the I–III line at the triple point to be 0.0195; I find above 0.0140. The slope of the II–III line Tammann gives as -0.75, and I find it to vary from $-.415$ to $-.273$. At the triple point Tammann gives for the change of volume (uncorrected) of II–III, 0.0205, and for I–III, 0.0115, against 0.0241 and 0.0140 above (corrected). Tammann, however, had to leave an unexplained discrepancy of 7–10% in the ΔV values for II–III, the change of volume being different for the two directions of reaction.

For the values of $\Delta\alpha$, $\Delta\beta$, and ΔC_p, two methods of estimation are available. At the triple point the various quantities may be computed, and there are also experimental determinations of the difference of compressibility. Neither of these methods gives satisfactory results, however. The calculations at the triple point are uncertain because the variation of ΔV along the II–III line is so slight that even its sign is uncertain. The experimental values of the difference of compressibility are irregular and uncertain. We can, however, make the following rough statements at the triple point. I is more compressible than II, the difference being of the order of 0.0_65. The difference of expansion between I and II is very small and is uncertain as to sign. The specific heat of I is greater than that of II, and the difference is of the order of 0.3 kgm. cm. per gm. III is more compressible than I, and the difference is fairly large, of the order of 0.0_55, but there is a good deal of uncertainty as to the numerical value of this difference. III is less expansible than I, the difference being of the order of 0.0_44 and III has a smaller specific heat than I, of the order of 0.3. From these values, of course, the differences between II and III may be found immediately by a subtraction.

In addition to these very rough values at the triple point, there have been several other determinations at atmospheric pressure. It has been shown directly that the relations of I and II are abnormal both in regard to expansion and specific heat. The form II has a negative coefficient of expansion. We have no accurate measurements of it at the transition point. The best are by Fizeau [19] on crystals. He found at 40° for large crystals the average contraction of 0.0_648 and for the precipitated salt by a dilatometric method 0.0_674 cm³./gm. (I have taken the density at room temperature as 5.67 from data of Rodwell [15]). Fizeau and Rodwell have both shown, however, that the coefficient increases rapidly with rise of temperature. Rodwell's data would give an average coefficient between 70° and 150° of -0.0_535. From data of Rodwell we also find that the mean expansion of I between 150° and 450° is about 0.0_55. These measurements of the expansion are too uncertain to justify us in making calculations of the difference. The data for specific heat are somewhat more concordant. Two observers agree in finding that I has a smaller specific heat than II. At the transition point Bellati and Romanese [16] give for the specific heat of I 0.0577 cal. and for that of II 0.0654, making a difference of 0.0077 cal. Mallard and Le Chatelier [17] give for the specific heat of I between 154° and 347° 0.055, and for II between 20° and 127°, 0.059. Since however, they estimate the accuracy of the individual measurements as only 3%, we evidently cannot place much reliance on their difference. If we assume the value of Bellati and Romanese for the difference and combine with the values given above for $\dfrac{d\Delta V}{dp}$ $(= -0.0_653)$ and $\dfrac{d\Delta H}{dp}$ $(= 0.005)$, we find $\Delta\beta = -.00002$, whereas we know $\Delta\beta$ to be positive. If $\Delta\beta$ is to be positive with the above values for $\dfrac{d\Delta V}{dp}$ and $\dfrac{d\Delta H}{dp}$, the difference of specific heats must be at least twice as great as it is. We can get a much better value for $\Delta\alpha$. If we assume $\Delta\beta = 0$, and it evidently is very small, we find $\Delta\alpha$ is of the order of 0.0_65, the same as found above at the triple point. We may accept this value with some confidence therefore. Combined with the value of Richards and Jones [20] for the compressibility of the ordinary variety, this means that I is about twice as compressible as II, although it has the smaller volume. The

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[19] Fizeau, Pogg. Ann. **132**, 292 (1867).
[20] T. W. Richards and G. Jones, Jour. Amer. Chem. Soc. **31**, 158–191 (1909).

indications are that the difference of specific heat between I and II changes sign along the transition line; at atmospheric pressure I has the smaller specific heat, but at the triple point that of II is the smaller. It must be insisted, however, that all these values are exceedingly rough; $\dfrac{d\Delta V}{dp}$ and $\dfrac{d\Delta H}{dp}$ are not given at all accurately by the above data.

No other modifications were found to 12000 kgm. at either 20° or 200°.

The form of I is cubic and that of II hexagonal, but the two forms are very little different.

MERCURIC IODIDE. This substance is the only one found so far which shows a maximum transition temperature between two solids, a result both unexpected and important. A great deal of time was spent on this substance in order to exhaust every other possible ex-
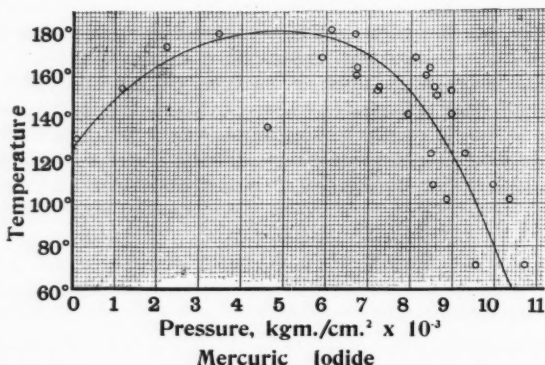

Mercuric Iodide

FIGURE 24. Mercuric Iodide. The observed equilibrium temperatures and pressures. It was not possible for this substance to shut the equilibrium conditions within narrow limits, and in the figure the limits of the reaction are shown. The text should be consulted for further particulars.

planation of the effects, and to establish this result beyond doubt. It is particularly difficult to get accurate results for this substance, because of the unusually wide region of indifference. The interpretation of the earlier results was also obscured by occasional leaks through a minute flaw in the cylinder; this flaw was due to amalgamation

produced by mercury set free by decomposition, in the presence of steel, either of the HgI$_2$ of this experiment, or of other mercury salts used in previous experiments.

The HgI$_2$ was obtained from Eimer and Amend, "c. p." and was used without further purification. For the first runs it was hammered cold into a thin steel shell, and pressure transmitted directly to it, by kerosene. After this first run small transverse holes were drilled through the sides of the shell to facilitate the reaction, and cut down the width of the band of indifference, but no effect from this could be observed. For the later runs, the HgI$_2$ was initially melted into the steel shells and then the lateral holes drilled. No effect of the greater initial compactness in increasing the reaction velocity was to be
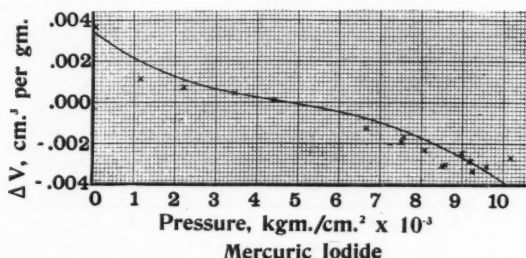

FIGURE 25. Mercuric Iodide. The observed differences of volume.

observed. Three different samples were used, from 86 to 100 gm. in amount, but each of these samples was used for a number of settings up of the apparatus, and one was used for both high and low pressure measurements. The effect of pressure is to compact the HgI$_2$ into a mineral like mass, without the slightest tendency to dissolve in the kerosene. After long use a slight amount of decomposition with setting free of minute globules of metallic mercury could be detected where the surface of the HgI$_2$ comes in contact with the steel. This is to be expected, because iron will deposit mercury from mercury salts, but the decomposition was too slight to produce a perceptible change in the total volume of the reacting quantity of HgI$_2$.

In view of the importance of the maximum temperature exhibited by this substance, a detailed description of the experiment will be given. When I started to investigate this substance, all that I knew about it was that it had a transition at atmospheric pressure at 127°,

the red form changing to yellow at this temperature, and that presum-
ably the yellow had the larger volume, so that the transition line would
rise with increasing pressure.   It will be easier to follow the descrip-
tion of the many runs made with this substance to turn at once to the
phase diagram of Figure 24.   The first run was made at room tempera-
ture, and no transition was found to 12000.   Temperature was then
raised to 150°, and transition found at about 8000 with very wide limits
of indifference.   Other points were then found at 108°, 141°, 159°;
the pressure limits are indicated in the diagram.   Temperature was
then raised to 200°, and no trace whatever of the transition could be
found between 12000 and 700.   Pressure was then raised to 6800, and
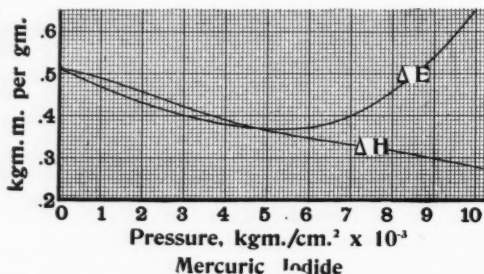temperature reduced to 160°, but no transition could be found down

FIGURE 26.   Mercuric Iodide.   The computed values of the heat of transi-
tion and the change of internal energy

to 700.   This was difficult to explain.   What had become of the
transition found at lower temperature and also of that at atmospheric
pressure at 127°?   On starting again at room temperature, raising
pressure to 8400 and temperature to 162°, the transition was found
again where expected, but on raising temperature to 180°, the transi-
tion disappeared.   Another run at 185°, however, indicated a transi-
tion at 9600, but this was later traced to leak.   Several other curious
effects between 160° and 200°, and 8000 to 12000 kgm. were also later
traced to leak, but were at first thought to be due to another transition.
At this stage the most plausible explanation seemed to be a rising
transition curve from 1 kgm. and 127° to about 7500 and 160°, and
here a triple point with the curve found below 160°, and the supposed
curve above 160°.   To test this, temperature was raised from 126°

to 153° at 2200 kgm., but no transition line was found. Again the question, what had become of the line starting at 127°? Very shortly after this the flaw in the cylinder grew to visible size, a new cylinder was made, the mysterious points found before at high temperatures and pressures disappeared, and the correct explanation of the effects was found.

In brief, the curious effects are due to a transition curve with a maximum, combined with a region of indifference of unusual shape. This region is indicated by the circles in Figure 24, which mark the

TABLE XI.

MERCURIC IODIDE.

Pressure	Temperature	ΔV cm³./gm.	$\dfrac{dt}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
1	127°.0	.00342	.0267	.513	.513
1000	149 .8	217	187	.491	.469
2000	165 .2	127	122	.456	.431
3000	174 .9	065	069	.420	.400
4000	179 .9	024	028	.390	.380
5000	181 .2	− 008	− 010	.365	.369
6000	178 .2	− 045	− 059	.345	.372
7000	169 .7	− 100	− 134	.330	.400
8000	152 .4	− 175	− 234	.318	.458
9000	122 .3	− 270	− 361	.296	.539
9500	102 .4	− 325	− 427	.286	.594
10000	79 .4	− 390	− 495	.278	.668

experimentally determined limits of this region; the transition curve is drawn through the mean points. We see that the region of indifference is of different shape on the two branches of the curve. If HgI_2 is heated at atmospheric pressure, the red changes to yellow pretty sharply on passing through 127°, but on cooling again, the yellow may persist for several hours, even at room temperature. That is, the red cannot be much superheated, but the yellow can be very considerably subcooled. With increasing pressure and temperature, the shape of the region changes as indicated, until on the descending branch of the transition line, the equilibrium may be overpassed in either direction, but to a very much less extent than at atmospheric pressure. This

shape of the indifferent region makes it impossible to obtain equilibrium values on the ascending branch by shutting the pressure within two limits approached from above and below.   The best that could be done here was to use the method of varying temperature at constant volume, varying the temperature by small steps, and relying on the relatively small amount of superheating to get a fairly good value for the transition temperature.   The change of volume can be determined from these data by methods already used.   Evidently the failure of this method to give any results at 2250 kgm. on the first trial mentioned above was because the temperature was not raised sufficiently high.

The shape of the region of indifference gives rise to curious effects in the neighborhood of the maximum.   Thus at room temperature, the pressure was once raised to 6500, the temperature was then raised to 165°, and pressure was raised, with a transition at the expected place, but on releasing pressure no reverse transition was found on crossing either branch of the curve.   The location of the indifferent region evidently explains this.   On another occasion, temperature was raised at 6600 completely through the indifferent band, the transition running as to be expected on emerging at 180°, but on lowering temperature to 175° and reducing pressure, no reverse transition could be found.

The existence of the maximum was further established by the following runs.   First, temperature was raised to 190° at about 2500 kgm., giving the regular transition point at about 165°.   At 190°, pressure was increased to 10,000 with no transition; at 10,000 temperature was lowered to 120° with no transition, and at 120° the transition was found again at the point to be expected on lowering pressure. Again, starting at 120° and 9000 kgm., temperature was raised to 195° with the transition at the expected point; at 195° pressure was lowered to 4600 with no transition; at 4600 kgm. temperature was lowered in steps of 10° to 120°, passing a transition with almost imperceptibly small change of volume at 134°, which therefore marks the lower limit of the indifferent region, and at 120°, pressure was raised again, the volume returning to its initial value when the initial pressure was reached.   To make still more certain that the initial conditions had been recovered, pressure was increased beyond its initial value at 120°, and the regular transition found both from above and below.   That is, we have here the experiment of describing a complete circuit and coming back to the starting point, with practically only one discontinuous change of volume.   If the pressure of decreasing

temperature had been chosen a little higher than 4600, so as to exactly equal the maximum, no trace of a second transition would have been found.

The existence of the maximum involves properties that at first sight seem so unnatural, that perhaps this elaborate procedure to establish it has been worth while.   A maximum would seem unlikely because at this point the change of volume is zero; at lower pressure the high temperature form with the larger volume is the more compressible, which is of course natural, but at pressures higher than the maximum, the high temperature form has the smaller volume and a higher compressibility than the low temperature phase.   Now this peculiar relation of the compressibilities was shown by experiment to actually exist.   On the falling branch of the curve, the compressibility of the phase with the smaller volume was the higher. · This could be determined from the difference of the slope of the volume isothermals above and below the transition.   Some attempt will be made later to find the magnitude of this difference; it cannot be determined accurately, but the fact is absolutely beyond question. This curious relation of the compressibilities is not an absolutely new thing; it is shown by ice and water, but there the explanation is probably to be found in the greater rigidity of the crystalline framework as contrasted with the structureless liquid.

Regarding the accuracy of the results, the values given here are probably more irregular than those for any other substance which does not decompose.   The explanation, of course, is the great width of the band of indifference, and the sluggishness of the reaction.   The irregularities in the ΔV values are considerably greater than in the values for pressure and temperature.   The values of ΔV probably have their greatest error on the rising branch of the curve.   The ΔV curve as shown was so drawn as to nearly pass through the directly determined value at low pressure, and also to pass through zero at the pressure of the maximum temperature.

In spite of the abnormally wide band of indifference, the pressure approached a stationary value after the reaction had once started as rapidly for this as for many other substances; the usual time for reaching a stationary pressure being only about 15 minutes.   This suggests most strongly that there is no direct connection between the width of the band of indifference and the velocity of reaction; there seems every reason to think that even in infinite time the apparent width of the band of indifference would not become materially less.

There are no other values at high pressures for comparison.   The

value 127° was adopted for the transition point at atmospheric pressure. This could be safely done without making a redetermination of it for this special sample, since this value is certainly as accurate as the other values at high pressures.   There are a number of measurements at atmospheric pressure.   For the transition point we have 127.2° by Reinders,[4] 127° by Steger,[18] 130° by Guinchant,[22] and Schwarz[8] gives the limits 124.5° to 130.2° by a thermal method, and 126.3° to 129.3° by an optical method.   There is one value of the change of volume, 0.00135 cm³ per gm. by Reinders,[21] against 0.00342 found above.   It would seem that the larger would be more likely to be correct.   For the latent heat there is the value 3.0 cal per gm. by Berthelot, as quoted by Varet,[23] and 1.53 cal. by Guinchant,[22] as against 1.2 cal. calculated above.   If a smaller value of the change of volume were used, the calculated value of the latent heat would be smaller.

We have already seen that at a maximum point the relations between the compressibilities and thermal expansions of the two phases may be deduced from the curves for Δv and ΔH, the specific heat disappearing from the relations at the maximum point.   These values at the maximum are included in the following.   It has also been stated that direct measurements of the difference of the compressibility showed that above the maximum the phase of smaller volume has the larger compressibility.   The numerical value of the difference could not, however, be determined with much accuracy.   Within the limits of accuracy, $\Delta \alpha$ would seem to be constant on the falling branch at 0.0_633 cm.³ per gm. per kgm. per cm².   Seven determinations of this quantity were made; the deviations of the several values from 0.0_633 are; $+35\%$, -15%, 0%, -25%, 0%, -60%, and 0%.   The deviations are large, but still this is as accurately as one can hope to get quantities as small as these by a method like the above.   This value is also not inconsistent with that deduced from the ΔV curve at the maximum point, where we have already seen that $\Delta \alpha$ is determined by the ΔV curve alone.   It was not possible to make any measurements of $\Delta \alpha$ on the rising branch of the curve.   If, however, we make the assumption that $\Delta \alpha$ is constant on both branches of the curve (an assumption which is very doubtful) we may compute $\Delta \beta$ and ΔC_p on the two branches.   These values are given in Table XII, directly

[21] W. Reinders, ZS. phys. Chem. **32**, 494–536 (1900).

[22] J. Guinchant, C. R. **145**, 68–70 (1907).

[23] R. Varet, Ann. Chim. Phys. **8**, 79–141 (1896).

as computed, without any adjustment.   These figures would demand that HgI_2 be abnormal in many respects.   On the rising branch of the curve the yellow modification is less expansible than the red, but above 6000, on the descending branch, the yellow becomes more expansible. The place at which $\Delta\beta$ changes sign need not necessarily coincide with the maximum.   In general, however, the phase with the smaller volume, whether at the higher or lower pressure seems to have the higher thermal expansion. ΔC_p calculated in accordance with the assumption above as to $\Delta\alpha$ comes out negative, the yellow having the smaller specific heat.   But it has already been shown that ΔC_p is particularly sensitive to errors in the assumed value for $\Delta\alpha$, and in

TABLE XII.

MERCURIC IODIDE.

Pressure	$\Delta\beta$	ΔC_p
1	$-.0_4 38$	-1.50
2000	$-.0_4 36$	-1.73
6000	$+.0_4 20$	-1.31
8000	$+.0_4 23$	-0.43
10000	$+.0_4 21$	-0.18

this case there is a direct determination of the specific heat by Guinchant, from which it appears that the yellow at atmospheric pressure has the larger heat, the difference being 0.0040 cal.   At higher pressures, ΔC_p calculated with the assumption as to $\Delta\alpha$, decreases rapidly. Combining this with the experimental value at atmospheric pressure, we are probably justified in the conclusion that the difference of specific heats becomes less at high pressures.   The sign of $\Delta\beta$ found above was verified by direct measurement on the rising branch of the curve, but the direct measurements did not give regular numerical results.

PHENOL.   This was Kahlbaum's purest, further purified by crystallization at constant temperature in the thermostat.   Two lots were purified; the first was pure white in color, and the second was very

slightly pinkish, but it had a melting point 0.02° higher than that of
the first lot, and a trifle higher than any previously recorded for
phenol. The purity is apparently, therefore, as great as can be
obtained by ordinary means. The pinkish specimen was used for
the high pressure determinations. This specimen was not perfectly
pure, however, because some rounding of the corners could be detected.
It was melted into the inverted steel shell and pressure transmitted
to it by mercury. Four different fillings of the apparatus were used;
one for the point at low pressures and the other three for the points
at high pressures. The quantities used varied from 13.5 to 17.5 gm.
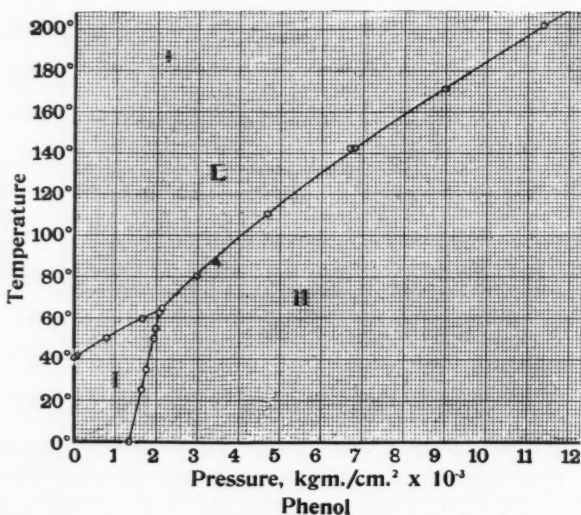

FIGURE 27.   Phenol.   The observed equilibrium temperatures and pressures.

The experimental values of pressure and temperature are shown in
Figure 27, the experimental values of ΔV in Figure 28, the computed
values of ΔH and ΔE in Figure 29, and the numerical values are col-
lected in Table XIII.   No points have been discarded.

It has been known for some time that phenol has two modifications.
These were discovered by Tammann,[24] who has written two papers on

24 G. Tammann, "K. und S.," 308, and ZS. phys. Chem. **75**, 75–80 (1910–
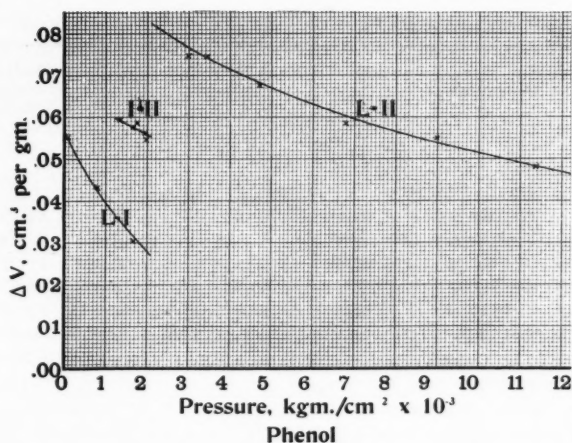11).

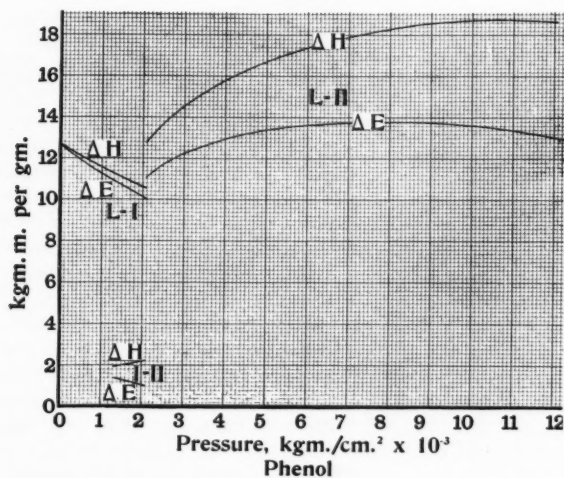FIGURE 28. Phenol. The observed differences of volume between the several phases.

FIGURE 29. Phenol. The computed values of the heats of transition and the change of internal energy.

TABLE XIII.

Phenol.

Pressure	Temperature	ΔV cm³./gm.	$\dfrac{dt}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
		Liquid — I.			
1	40°.87	.0567	.0140	12.70	12.70
500	47 .5	471	125	12.12	11.88
1000	53 .4	395	111	11.62	11.22
1500	58 .7	335	099	11.15	10.73
2000	63 .3	280	088	- 10.72	10.16
		I–II.			
1327	0°.0	.0593	.0843	1.926	1.139
1565	20 .0	580	"	2.021	1.113
1803	40 .0	568	"	2.113	1.089
2039	60 .0	556	"	2.202	1.068
		Liquid — II.			
2000	62°.1	.0831	.02218	12.56	10.90
3000	82 .1	767	1868	14.58	12.28
4000	99 .8	714	1684	15.81	12.95
5000	115 .9	669	1553	16.75	13.40
6000	131 .0	630	1461	17.42	13.64
7000	145 .2	595	1389	17.92	13.76
8000	158 .8	564	1334	18.26	13.75
9000	171 .9	538	1289	18.58	13.74
10000	184 .6	513	1254	18.73	13.60
11000	197 .0	489	1228	18.72	13.34
12000	209 .2	468	1211	18.64	13.02
		Triple Point.			
2085	64°.0	L–I .0270	.00861	10.57	10.01
		L–II .0825	.02171	12.79	11.07
		I–II .0555	.0843	2.221	1.063

it.   The pressure range of the results given here is considerably greater than that of Tammann, but Tammann's temperature range on the I–II curve is more extensive.   Tammann's second paper is almost exclusively occupied with the lag phenomena on the I–II curve.   He finds that the band of indifference grows rapidly wider at the lower temperatures, becoming so wide at liquid air temperatures that II may be realized at atmospheric pressure.   In this work, the same qualitative behavior of the band of indifference was found.   At 0° the width of the band was 180 kgm.; at 25°, 80 kgm.; at 35°, 50 kgm.; at 50°, 20 kgm.; and between 57° and 62° no difference could be detected in the pressures reached from above and below.   From one of Tammann's diagrams I should estimate the width of his band to be about 350 kgm. at −10°, 200 kgm. at 0°, 50 kgm. at 10° and above 30° the scale of his diagram does not allow an estimate.   Apparently the width of his band decreases with rising temperature more rapidly than mine. This emphasizes that too little is known at present of the various factors which determine the width of the band to allow us to attach significance to the absolute width of the band when measured under different conditions.

Tammann's transition line I–II showed one other remarkable feature in that at the upper end it rises much more rapidly than it does at the lower temperatures.   Tammann's substance was somewhat impure, as he himself recognized, so that it was questionable how much of the curvature could be laid to the account of the impurity, but Tammann suggested that it might be found that for the pure substance the transition line would pass through a vertical position, and consequently the latent heat through a zero value, before reaching the triple point.   In the effort to settle this question, I made careful measurements of the transition coördinates between 50° and the triple point; these are reproduced on a much enlarged scale in Figure 30.   It is seen that no point departs from the straight line (this is the same straight line which passes through the low temperature points) by more than 3 kgm., which is the limit
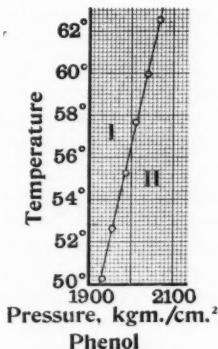

FIGURE 30. Phenol. Points on the upper end of the transition line I–II on a very much enlarged scale. There is no curvature appreciable.

of sensitiveness of the pressure measurements. We conclude, therefore, that the transition line rises to the triple point with no perceptible change of direction, and that the curvature found by Tammann must have been an effect of the impurity.

Tammann determined the phase diagram with two specimens, one somewhat purer than the other. In the following comparison of his results with those found here only the data of his pure sample will be used. His L–I curve is 0.3° lower than mine at atmospheric pressure, and 1.2° lower at 2000. At 20° his I–II line is 50 kgm. higher than mine, and 4 kgm. lower at 60°; this is an effect of the curvature found by Tammann. Above the triple point, his L–II curve runs lower than mine and with a smaller slope; at 2600 it is about 3° lower. He finds as the coördinates of the triple point 2196, kgm. and 62.8° against 2085 and 64.0° of mine. The discrepancies are at least in part due to impurity. Tammann's value for ΔV at atmospheric pressure, 0.0463, is much lower than mine; he recognizes that his value is too low, due to impurity. His value for ΔV, I–II, is also very much lower than that found here, 0.0315 against 0.0568 at 40°. Curiously, however, his value for ΔV, L–I, at the triple point is almost exactly that found here, 0.0273 against 0.0270.

Besides Tammann's values at low pressures there are also a number of other values for comparison. Hulett[25] has measured the effect of pressure on the melting point up to 300 kgm. He finds for the melting point 40.75° against 40.87° above, and for the initial slope 0.0149° per kgm. against 0.0140 above. It should be remarked that the value of Hulett for the melting point is sometimes misquoted as 41.11°, because of a misprint in the original paper by which the melting point under 25 kgm. is given twice, once as that at atmospheric pressure. Other values for the melting point are 40 to 41° by Calvert, quoted by Schiff,[26] and 42.5° to 43° by Behal and Choay[27] for a specimen of phenol synthesized by a new method. For the change of volume we have 0.054 to 0.051 by Heydweiller[28] and 0.0532 by Block[29] against 0.0567 above. For the latent heat, there is 24.93 cal. by Pettersson and Widman,[30] and 26.9 cal. by Eykmann,[31] against 29.7 above.

[25] G. A. Hulett, ZS. phys. Chem. **28**, 629-762 (1899).
[26] R. Schiff, Lieb. Ann. **223**, 247–268 (1884).
[27] A. Béhal and E. Choay, Bull. Soc. Chim. Paris, (3) **11**, 602–603 (1894).
[28] A. Heydweiller, Ann. Phys. **61**, 527–540 (1897).
[29] H. Block, ZS. phys. Chem. **78**, 384–426 (1912).
[30] O. Pettersson and O. Widman, Förh. Stock. (3) **36**, 75–79 (1879).
[31] J. F. Eykman, ZS. phys. Chem. **4**, 497–519 (1889).

There are three different methods of attack on the values for the difference of compressibility, expansion, and specific heat for this substance. In the first place, a direct measurement of the difference of thermal expansion of the liquid and the solid I was possible at low pressures. The phenol was so pure that the rounding of the corners was very slight, and this value ought to be fairly good. Then direct measurements were made of the difference of compressibility of I and II along the transition line. These values are fairly good, especially at the lower temperature. And finally, at the triple point, we have theoretically the means to calculate all the differences between the two phases. But actually the various derivatives are not known accurately enough to permit this calculation at the triple point. For instance, a rigorous solution of the six equations at this point demands that I is less compressible than II, whereas direct experiment shows that it is more compressible. The values follow. At 77 kgm. the liquid is more compressible, more expansible and has a greater specific heat than I, as follows:

$$\left.\begin{array}{l} \Delta\alpha = 0.000025 \\ \Delta\beta = 0.00027 \\ \Delta C_p = 6.9 \,[\text{kgm. cm./gm.}] \end{array}\right\}$$

$\Delta\beta$ was found by direct experiment and the others were computed. The value found by Block [29] for $\Delta\beta$ is considerably less than that found here, 0.00017 against 0.00027.

At the triple point it was established by direct experiment that I is more compressible than II. The difference of compressibility increases somewhat at the lower temperatures. At the triple point the difference is of the order of 0.000005. The difference of compressibility between liquid and I calculated from this is about 0.0_415. This value may probably be counted on with some certainty because it is not much affected by changes in the value of $\Delta\alpha_{12}$. The differences in expansion between the two phases are, however, very susceptible to errors in the compressibility. One cannot conclude with certainty which of I or II is more expansible. The liquid is certainly more expansible than I and the difference is of the order of 0.0002. More than this cannot be stated. The differences of specific heats between the liquid and the two solids are also very susceptible to slight errors; small changes in the constants may change the sign. The difference of specific heat between the two solids is not so sensitive, however, and it seems fairly certain that the specific heat of I is lower than that of II, perhaps a surprising result. The difference is small, and of the order of 0.3 kgm. cm. per gm.

No other modifications of the solid were found to 12000 at 25°. or to 12500 at 200°.

URETHAN.   This was obtained from Eimer and Amend, and further purified by crystallization at constant temperature in the thermostat. Beautiful, colorless, transparent crystals were obtained, columnar in form, some of them 2 or 3 inches long.   The melting isothermals showed very little rounding of the corners, so the purity must have been fairly high.   A remarkable property of the crystals is their great flexibility; they may be bent in the fingers like paraffine.   It is possible that this may be due to twinning, as in the case of calcite;
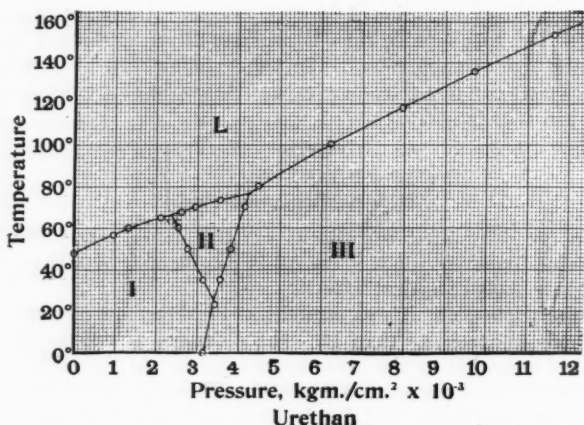

FIGURE 31.   Urethan.   The observed equilibrium temperatures and pressures.

it would be an interesting subject for investigation.   Two fillings of the apparatus were used.   The first gave the low pressure point and nine points at higher pressures.   After this, the splitting of the steel shell necessitated the using of another sample, with which twelve points at high pressures were obtained, completing the phase diagram. The quantities used were 17 and 13.5 gm.   The urethan was melted into the inverted nickel steel shell and pressure transmitted to it by mercury.

Two new solid modifications were found; these are so situated in the phase diagram that all the triple points and equilibrium lines

possible for a four phase system actually exist; six equilibrium lines and three triple points. The experimental values for pressure and temperature are shown in Figure 31, the experimental values of ΔV in Figure 32, the computed values of ΔH and ΔE in Figure 33, and the
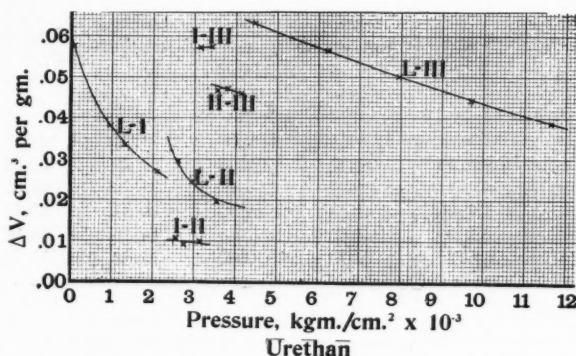

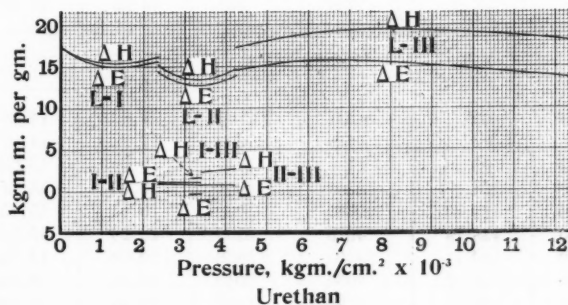FIGURE 32. Urethan. The observed changes of volume.

FIGURE 33. Urethan. The computed values of the heats of transition and the changes of internal energy.

numerical values are given in Table XIV. It was necessary to discard two points in the immediate neighborhood of the L–I–II triple point, which were determined before it was known that there was a triple point here. The three melting curves are entirely normal.

TABLE XIV.

Urethan.

Pressure	Temperature	ΔV cm³./gm.	$\frac{dt}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
Liquid — I.					
1	47°.90	.05990	.01105	17.39	17.39
500	53 .0	4620	0940	16.03	15.80
1000	57 .3	3762	0840	15.54	15.17
1500	61 .0	3182	0688	15.46	14.98
2000	64 .2	2774	0592	15.82	15.27
Liquid — II.					
2500	67°.3	.03130	.00738	14.70	13.92
3000	70 .6	2384	603	13.59	12.87
3500	73 .4	2026	519	13.53	12.82
4000	75 .8	1880	461	14.23	13.48
Liquid — III.					
4500	80°.3	.06294	.01263	17.62	14.79
5000	86 .5	6110	1202	17.98	14.97
6000	98 .0	5724	1114	19.06	15.63
7000	108 .7	5354	1053	19.42	15.67
8000	119 .0	5000	1008	19.45	15.45
9000	128 .9	4670	0969	19.28	15.08
10000	138 .4	4350	0938	19.00	14.65
11000	147 .7	4056	0913	18.69	14.23
12000	156 .7	3780	0887	18.32	13.78
I–III.					
3160	0°	.0572	.1040	1.504	− .309
3260	10	573	"	1.561	− .307
3350	20	574	"	1.617	− .306

I–II.

3280	30°	.00930	− .0392	.719	1.024
3030	40	952	"	.760	1.048
2770	50	976	"	.804	1.074
2520	60	999	"	.849	1.101

II–III.

3470	30°	.04800	.0612	2.376	.711
3640	40	4748	"	2.429	.701
3800	50	4696	"	2.479	.695
3960	60	4644	"	2.527	.687
4130	70	4592	"	2.574	.677

TRIPLE POINT, LIQUID — I–II.

		L–I .02530	.00530	16.19	15.59
2350	66°.2	L–II .03550	.007866	15.31	14.48
		I–II .01020	− .0392	.883	.112

TRIPLE POINT, LIQUID — II–III.

		L–II .01840	.00438	14.70	13.91
4230	76°.8	L–III .06396	.01300	17.32	14.61
		II–III .04556	.0612	2.61	.68

TRIPLE POINT, I–II–III.

		I–II .00922	− .0392	.702	1.015
3400	25°.5	II–III .04820	.0612	2.352	.713
		I–III .05742	.1040	1.650	− .303

The transition line I–II is somewhat unusual in that ΔV increases with increasing temperature.

The band of indifference shows interesting variations. On each of the three curves, I–III, I–II, and II–III, the band decreases in width with increasing temperature; but besides the general effect of temperature, there is a very marked specific effect of the nature of the reacting phases. Both the bands I–II and II–III are broader at their lower ends than I–III is at its upper end, although the temperature of the lower end of the first two bands is the same as that of the upper end of the I–III band. The actual widths are as follows. I–III is 200 kgm. wide at 0°, and 60 kgm. wide at 25.2°; I–II is 250 kgm. wide at 35.3°, 75 kgm. at 50°, 20 kgm. at 58°; II–III is 60 kgm. wide at 35.3°, 20 kgm. at 50°, and 3 kgm. at 70.2°. Along with this change in the width of the band there goes a parallel change in the reaction velocity. No trouble was ever found in forcing the desired reaction to take place; but no observations were made of the precise amount of subcooling or superheating. It was observed once at 50° that I had to be carried 650 kgm. across the line before II appeared.

No other transitions were found to 12700 kgm. at either room temperature or 153°.

The effect of pressure on the melting point of urethan has also been measured by Tammann,[32] who did not find any other modifications. Tammann's pressure range was to 2905 kgm. At the upper end of the melting curve he must therefore, have had the modification II without knowing it. Tammann remarks that below 1500 kgm. the melting curve is parabolic, but that above 1500 it is nearly linear; this linearity is evidently the effect of the overlooked transition. In fact, if one plots Tammann's points, he will find some evidence for the change in direction of the curve above the triple point, although the points are rather irregular. Tammann also looked for other modifications of the solid out to 3000 kgm. at 40°; if he had tried 60° instead, he would probably have found II. The melting point at atmospheric pressure was 48.14° against 47.90° above. The presumption from this alone would be, therefore, that Tammann's specimen was purer than mine. But at high pressures his curve drops below mine, being 1.8° lower at the upper end, and he also states that the reaction was unusually slow for a melting reaction. Both of these points suggest impurity. In the work above, the melting set in as rapidly as for any normal liquid. It almost seems as if the design of Tammann's apparatus had been

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[32] G. Tammann, "K. und S.," p. 239.

such as to permit the comtamination of the liquid at high pressures. Tammann finds for ΔV at atmospheric pressure 0.0573, and at 1455 kgm. 0.0378, against the corresponding values 0.0599 and 0.0322. The agreement at atmospheric pressure is comparatively good, but it is unusual that the discrepancy should be in the direction it is at high pressures.   Other values for comparison are 47° to 50° for the melting point by McCreath,[33] and 48.5° by Block.[29]   Block gives for the change of volume 0.0576.   For the latent heat there is 40.8 cal. by a direct method and 41 by a cryoscopic method by Eykmann.[31]   The value found above, 40.8, is in unusually good agreement.

Urethan has three triple points at each one of which the difference of compressibility etc. between the phases can be calculated.   The data are not accurate enough, however, at the two triple points involving the liquid to give accurate results.   Thus a solution of the equations at the triple point L–I–II demands that I be very much more expansible than the liquid, which seems very unlikely.   Probably a large part of the error is occasioned by the abnormally rapid change of slope of the ΔV curve for L–II.   The only information of value is, therefore, that given at the triple point I–II–III.   We find on solving the six equations at this point the following values,

$$\Delta\alpha_{12} = 0.0_511$$
$$\Delta\alpha_{23} = 0.0_411$$
$$\Delta\alpha_{13} = 0.0_412$$
$$\Delta\beta_{12} = -0.0_55$$
$$\Delta\beta_{23} = 0.0_3135$$
$$\Delta\beta_{13} = 0.0_3130$$
$$\left.\begin{array}{l}\Delta C_{p12} = -0.127 \\ \Delta C_{p23} = 0.43 \\ \Delta C_{p13} = 0.30\end{array}\right\} \text{ kgm. cm./gm.}$$

There is doubtless a large amount of uncertainty in these numerical values; probably $\Delta\alpha_{23}$ is too large, and $\Delta\beta_{12}$ too small.   The signs of the quantities are of interest.   The compressibilities follow the order of volumes, as we should expect, and the specific heats the order of temperatures.   Thus as we raise temperature at constant pressure we may change III to I, and then I to II.   On passing through each of these transitions the specific heat increases.   As regards the thermal expansion, we do not know whether to expect the phase at the higher temperature or that with the larger volume to have the greater expan-

33 D. McCreath, Ber. D. Chem. Ges. **8**, 383–384 (1875).

sion.   We see that in this case the order followed is that of temperature. II is stable at a higher temperature than I and has the greater expansion, although it has the smaller volume.   I is more expansible than III, and II than III.

The difference of compressibility of the several solids as given directly by the difference of slopes was inappreciable.

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